Final Report of the Research Project:

"EFFECTS OF ACID RAIN ON PLANTS

AND SOILS IN CALIFORNIA"

Principal Investigator

Dr. John G. McColl
Associate Professor
Department of Plant and Soil Biology
University of California
Berkeley, CA 94720

ABSTRACT

Effects of acid rain on some California plants and soils were studied. Plants growing in soil were treated with simulated rain of varying acidity. Direct foliar damage was not apparent, other than under extreme conditions which are not normally experienced in the field. Sugar beet was the most sensitive of the agronomic species tested. Germination of Douglas-fir seed was inhibited under severe acid conditions. Similarly, growth of two-year-old conifer seedlings showed little deleterious effects, except under most severe treatments. Acid rain affected plant productivity (positively and negatively), and the effect for a given input acid was largely predicated by the soil in which the plants were growing. A simple, reliable laboratory method was developed for determining potential sensitivity of soils to leaching by acid rain. Silicic soils of low cation-exchange capacity, low base-saturation and shallow depth are most sensitive. Many granitic soils of the Sierra Nevada are sensitive because of their immaturity, geologic parent material, geographic location, and because possible remedial practices in these range and forest soils are impossible. Future research should focus on non-agronomic plants and soils on a long-term basis, on possible alteration of soil microbial processes, and on leaching of toxic elements from soils that may harm drainage waters.

ACKNOWLEDGEMENTS

DISCLAIMER

The statements and conclusions in this report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

SUMMARY AND CONCLUSIONS

Possible effects of acid rain on some California plants and soils were studied with particular attention given to plant productivity, interactions between plants and soils, and the leaching of soils.

Pot-trials were conducted with agronomic and forest tree species growing in representative soils. In the first trial, barley and clover were tested in unfertilized soil; productivity and detailed chemical composition of plant parts were determined following acid treatments ranging in pH from 5.6 to 2.0. Acid treatments were representative of those previously documented in California; the ratio of nitric acid to sulphuric acid was 3:2. In the second trial, barley, clover, sugar beet, soft chess and cabbage were tested in both unfertilized soil and in soil fertilized with nitrogen and sulfur; fertilizer salts were added to overcome any soil deficiencies of nitrogen and sulfur, and to enable direct effects of acidity per se to be identified. A third pot-trial with Douglas-fir and sugar pine in natural soil, was conducted using the same acid treatments, pH 5.6 through 2.0. A supplementary germination trial, using Douglas-fir and ponderosa pine seed was also carried out.

Tests were also made to determine relative sensitivity of a wide variety of California soils. Acid treatments were applied under strictly-controlled laboratory conditions, and soil leachates were chemically analyzed. The relative degree of soil leaching was used as an index of sensitivity.

The main results and conclusions of this research project are as follows:

1. Effects of acidic atmospheric precipitation on plants and soils vary greatly, depending on the nature of the input, the type of vegetation, the physical and chemical properties of the soil and its parent material, and natural production of acids.

2. Different plants react differently to acidic inputs. However, direct foliar damage to most plant species does not appear to occur unless acidity is extreme (beyond levels monitored in the field), but removal of leaf-surface waxes was documented in this study. Sugar beet was the most susceptible of the agronomic species tested.

3. Germination and very early growth of conifer tree-species are affected by relatively severe acidic inputs (pH 2). Germination percentage of Douglas-fir seed was reduced by 1/3 in the pH 2 treatment. Seedlings of both Douglas-fir and sugar pine treated with pH 2 inputs died soon after germination, due to susceptibility to fungal attack that does not normally occur.

4. Two-year-old Douglas-fir and ponderosa pine seedlings at the out-planting stage (i.e., from the nursery, ready for field-planting) were subjected to acid spraying during the spring bud-burst period. In the lowest pH-treatment (pH 2) , new needles had white acid-burns, brown tips, and the whole seedling became limp; symptoms became progressively worse, as needles (old and new) browned, died and dropped.

5. The interaction between plants and soil subjected to acidic input is of great importance. Acid inputs seriously affect plant productivity (positively and negatively), but the nature of the reaction for a given acidity of input is largely predicated by the soil in which the plants are growing.

In poor-fertility soil, plants generally grow better with increasing acidity of inputs within the acidity range of atmospheric precipitation

occuring in the field. This is because nitrogen and sulfur inputs increase simultaneously with increases in acidity, and these two nutrient elements act as fertilizers to increase plant productivity. Secondly, the acidity increases the availability of elements already in the soil (such as Ca, P, K) that are generally less-available in unacidified soil.

In fertilized soils, or those that are naturally more fertile, the "fertilizer effect" of acidic inputs is minimized, and the deleterious effects of acidity become more obvious, as shown by plant productivity. In short-term experiments, such negative effects are likely to be small when compared to the greater effects of the soil fertility alone on plant productivity. However, continued exposure of soil to acidic inputs would probably lead to decreased soil fertility, due to losses of available nutrients to drainage waters, and plant productivity would decrease accordingly.

6. Decreases in soil-pH enhances movement of toxic elements (such as Al and Mn). Al^{3+} is potentially harmful to plants, aquatic life, and soil microbial activity; any increases in Al^{3+} must be considered to be potentially deleterious.

7. A simple, reliable laboratory method has been developed for determining potential sensitivity of soils to leaching by acid rain. Combined with information about the geographical location and other elementary properties of the soil, this method can be used for accurately determining the relative sensitivity of soil from any area.

8. Different Californian soils react quite differently to acidic inputs. Leachate nutrient concentrations indicate orders-of-magnitude differences between soils. Calcareous and well-developed soils are unlikely to be seriously damaged by acid inputs, but leachates may be deleterious to the quality of groundwater and suface waters. Interactions between terrestrial

and aquatic systems dictate that conclusions from studies of soil studied in an isolated manner, must be considered carefully at the ecosystem level also. Soils that are silicic (e.g. granitics) with low cation-exchange-capacity, with low base-saturation and of shallow depth, are most susceptible to increased acidification. Many granitic soils of the Sierra Nevada are quite sensitive, because of their immaturity, geologic parent material, and geographic location.

9. Changes in soil-pH are most pronounced at the soil surface. With increasing time of exposure or severity of acidic input, effects occur progressively deeper in the soil profile.

10. Soils become acid both from acid rain and as a result of certain soil amendments and fertilizer practices. Acidification by the latter processes can be controlled by normal management practices in cultivated soils. However, large areas of California are not cultivated, and have soils that are poorly buffered and are, therefore, quite susceptible to accelerated acidification. Many of these soils occur in range and forest areas of the Sierra Nevada, where soil amendments or other remedial practices are impossible. These are also areas most water-catchments are located, and thus must be considered as areas that are most sensitive to acid rain.

RECOMMENDATIONS

1. Studies of the long-term effects of acid precipitation on soil leaching and plant productivitiy must be initiated.

2. More attention should be given to non-agronomic crops and soils. Many agronomic crops and soils can be suitably altered by various management practices to minimize effects of acid precipitation, whereas most areas of rangelands and forests are essentially impossible to manage for such effects.

3. More research should be conducted to elucidate effects of acid precipitation on microbial processes in the soil, and how alteration of these microbial processes affect plant productivity.

4. Leaching of nutrients and toxic elements from soil needs further study, not only from the viewpoint of the deterioration of the soil itself, but also because such leachates may affect drainage waters and aquatic life.

5. Relative effects of different compositions of acid precipitation on plants, soils and aquatic systems should also be given more attention. Specifically, effects of different ratios of nitric to sulfuric acids should be examined more closely.

6. Effects of temporal variation of acidic inputs on plant growth should also be studied, as most plants are susceptible to greatest damage in spring when the flush of succulent growth occurs, or at other specific periods of time such as when fruit is ripening. Similarly, effects of temporal variatons of inputs on aquatic life may be more important than averages may indicate.

7. Future research in California should focus on soils and plants of range and forested areas of the Sierra Nevada where rainfall is relatively high, the soils silicic (acidic) and shallow, and where streams and lakes could be affected by leaching of soils. These areas are potentially sensitive to acidic inputs and are not amenable to ameliorative management practices. Thus, recommendations 1-6 are particularly applicable to these foothill and mountainous areas of California which contain much of the State's water and timber resources, and which lie in the general area of atmospheric washout of air-pollutants from metropolitan areas.

INTRODUCTION

INTRODUCTION

Emissions of air pollutants resulting in acid rains, are now common phenomena in the northeastern U.S.A. (Likens, 1976), and also in Scandanavia where some of the earliest work in this area was performed (e.g., Barrett and Brodin, 1955). The acidity of rain has been increasing in the northeastern U.S.A. (Likens, 1976; Cogbill and Likens, 1974; Likens et al., 1979) and is having adverse ecological effects such as degradation of water-quality, fish productivity, and possibly forest productivity, and may also cause accelerated soil-leaching. Similar effects have been widely documented by Scandanavian workers who have taken the pioneering role in studying acid rain effects as well as monitoring acid deposition (e.g. Tollan and Overrein, 1978). The problem of acid rain in California has also been increasing for at least 25 years (McColl, 1981; McColl and Bush, 1978).

The literature in this field has proliferated in the last couple of years. However, the most up-to-date, relevant documentation is found in: 1) the Proceedings of an international conference on "Ecological impact of acid precipitation," that was held in Sandefjord, Norway (Drablos and Tollan, 1980); 2) the report by Cowling and Linthurst (1980) entitled, "Research on effects of acid precipitation in acquatic and terrestrial ecosystems," which outlines research conducted in the U.S. through grants by the Environmental Protection

Agency; 3) the National Acid Precipitation Assessment Plan (January 1981 draft) prepared by the U.S. "Interagency Task Force on Acid Precipitation" (1980); 4) the book by Hutchinson and Havas (1980); 5) the 1st acid rain Symposium Proceedings, edited by Dochinger and Seliga (1976); and 6) the final report of the 8-year, Norwegian research project on acid rain effects (Overrein, Seip and Tollan, 1980).

Two monitoring projects recently sponsored by the California Air Resources Board (Liljestrand and Morgan, 1978; Morgan and Liljestrand, 1980; McColl, 1980) have established that acid rain does occur in California and is quite widespread in its geographical distribution. In many locations monitored to date, most of the acid is HNO_3 derived for NO_x, and only about a third of the typical acidity is attributed to H_2SO_4 derived from SO_2. It is generally believed that most of the NO_x is from automobile exhausts in California.

Effects of acid inputs must now be investigated, as the potential loss of agricultural and forest productivity may be very great. Some factors controlling the fate of atmospheric precipitation in the soil-plant system are diagrammed in Fig. 1.

However, results of studies of effects on plants are not consistent (Jonsson and Sunberg, 1972; Lee et al, 1980; Tveite, 1975). Obviously different plant species have varying susceptibilities to increasing acidity of rain, and thus, experimental results vary accordingly (Evans et al., 1977). The same plant species growing in different soils, could also be affected differently by similar inputs of acid rain.

ATMOSPHERIC PRECIPITATION

DRY, Sea-salts
. Natural dust
Soil particles
Air pollutants
(gaseous and
particulates)

WET, Rain
Snow
Fog

rate, frequency
and distribution

———————————————— INTERACTION WITH
. VEGETATION

THROUGHFALL

LEAF LEACHING,
· of internal substances

LEAF WASHING,
of impacted particulates

———————————————— INTERACTION WITH
SOIL

SOIL WATER

SOIL LEACHING,
ion exchange and
nutrient loss

SOIL ABSORPTION,
ion exchange and nutrient
uptake by plants

————————————————
AQUATIC SYSTEM

Fig. 1. Some factors controlling the chemical characteristics of atmospheric
precipitation and the subsequent fate of water in the soil-plant
system.

Documentation of effects of acid rain on vegetation is difficult
as effects could be manifest in many different ways. Severe effects
would be easily visible, e.g., as indicated by marked decreases in
productivity, as necrotic spots on leaves, damage of meristematic
tissues, and even death of plants as a whole. More subtle effects
may not be visually apparent, and may only be observed with the aid
of more sophisticated equipment, e.g., it may be necessary to obtain
electromicrographs to identify cuticular damage of leaves due to
acid droplets. Evans et al (1977) used scanning electron microscopy
to diagnose damage to plants by acid rain, and noted lesions on
leaf surfaces, and even collapse of palisade cells. Even if plant
productivity is unaffected, removal of waxes on leaf-surfaces and
cuticular damage may result in increased sensitivity to plant dis-
eases (e.g., fungal infestation) and to damage by insects. Pesticide
sprays may also result in plant damage, if leaf surfaces had been
previously affected by acid rain inputs.

Experiments of effects of acid rain on soil have demonstrated
that increasing leaching of nutrients (such as calcium and magnesium)
usually occurs with increasingly acid precipitation (Abrahamsen, et al.,
1975; Bergseth, 1975; Overrein, 1972; Wiklander and Anderson, 1972;
Wiklander, 1973). Leaching of soils is usually limited by a lack of
anions (negatively charged) that are mobile in the soil (McColl and
Cole, 1968; Cole et al., 1975). Leaching occurs when hydrogen ions
(positively charged) are introduced along with mobile anions. In
polluted, "acid" rain, mobile anions are primarily those of sulfur

and nitrogen (both negatively charged, i.e. SO_2^{2-} and NO_3^-) which

are accompanied by an equivalent amount of hydrogen ions (i.e. acid

H^+ ions). Thus, the potential exists for increased soil leaching

due to acid inputs from a polluted atmosphere. The chemical mechanisms

for such reactions are explained in detail by Johnson and Cole (1977)

and Wiklander (1975), and shown in a simplified manner in Fig. 2.

Short-term increase in plant productivity could result from

increased availability of soil nutrients caused by acid inputs.

However, in most cases, increased soil leaching will result in reduced

plant growth, when leaching rates exceed the availability of nutrient

elements from other sources, such as weathering of minerals. Kuehn

(1972) in his thesis on "Acid Precipitation and Conifer Seedlings"

states that: "sulfur dioxide in the atmosphere is more damaging to

conifer trees than the associated sulfuric acid. However, there is

strong evidence to suggest that the long-range, indirect effects of

acid rainfall on conifer trees, such as those caused by a decreasing

soil pH and the associated changes in leaching rates and soil nutrient

availability could create a greater and more lasting potential for harm".

The effects of acid rain on microbially mediated nutrient reactions

in soil must also be considered.[1] Mineralization of soil organic matter

is a major source of N, S, and P, and the process of mineralization

is mediated by microbes. Alterations in the rate of organic matter

turnover could have enormous and long-term effects on the fertility

of the soil. All of the transformations in the soil controlling

---

[1]Effects of acid rain on soil microbiological processes are currently
being studied in a related research project by the author (Dr. J. G.
McColl) and Dr. M. K. Firestone, financed by the U.S.E.P.A.

INPUT: "Acid Rain"
$$HNO_3 + H_2SO_4$$
$$H^+ + NO_3^- + SO_4^{2-}$$

REACTION WITH SOIL:

Input solution

Soil sample

Leachate

H^+ displaces cations

LEACHATE: $Ca^{2+}, Mg^{2+}, K^+, Na^+$ with associated mobile anions, NO_3^-, SO_4^{2-} in solution.

SOIL AFTER LEACHING:
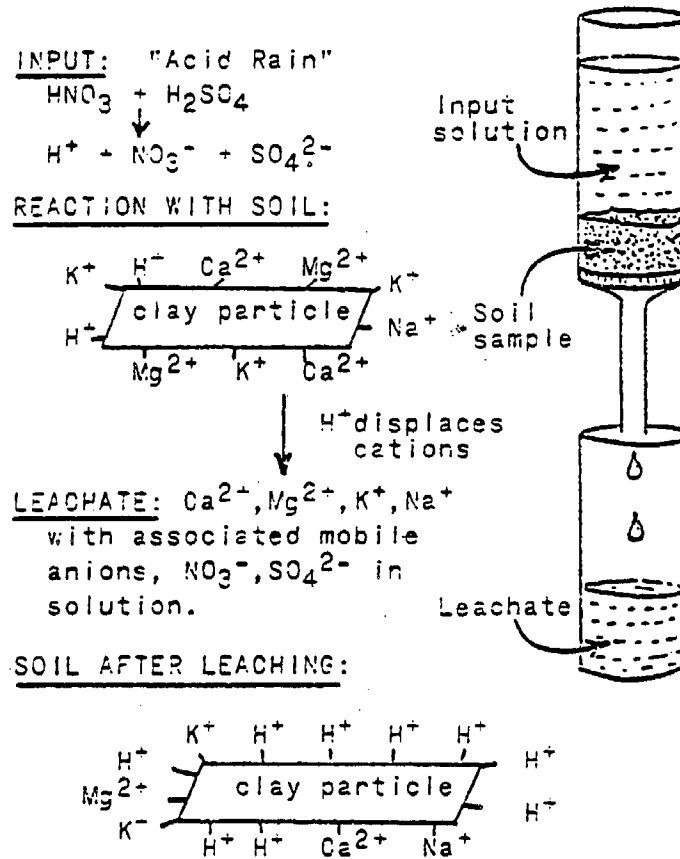
Fig. 2. Simplified mechanism of soil leaching by inputs of acid rain, and simplified diagram of apparatus used to measure the relative sensitivity of soils to acid rain inputs.

nitrogen availability to plants are microbially mediated. An effect on any of the nitrogen transformations occurring in the soil would alter the nitrogen availability to a plant growing in that soil.

The growth of the plant is a complex function of climatic conditions and nutrient supply by the soil medium. With this in mind it is somewhat surprising that several workers in this field study the effects of acid precipitation on plant growth while restricting the input only to plant foliage and avoiding input to the soil. The justification for this approach is that the system as a whole is far too complex to understand. Indeed, the whole plant-soil system is complex. However, the total soil-plant system receives the acid precipitation input in the real world. One cannot predict potential impact on plant growth without considering the effects of this input on the medium of plant growth, the soil.

The research reported here was designed to elucidate some of the effects of acid rain on plants and soil, and particular attention was given to the interactions between plants and soil. A series of three pot-trials were conducted, in which agronomic and forest species growing in soil were treated with simulated acid rain. In the first trial, two species (barley and clover) were tested in unfertilized soil. In the second trial, a total of five plant species were tested in both unfertilized soil and in soil fertilized with nitrogen and sulfur. In the third pot-trial, two forest-tree species (Douglas-fir and ponderosa pine) were tested in native soil. As a supplement

to the third trial with tree species, a germination experiment was conducted. In this experiment, seed of Douglas-fir and sugar pine were germinated under various acid rain treatments.

A separate series of tests were also conducted on soil alone, to determine relative differences in the effect of acid rain on leaching of important ions from a variety of California soils. The soils tested represented a range of soil conditions varying in age, geologic parent material, organic matter content, etc. Acid treatments were applied under strictly-controlled conditions, and consequent soil-leachates were chemically analyzed. The soils were then ranked, according to the relative degree of leaching, and thus their relative "sensitivities" to acid rain were determined.

In this report, these experiments are described separately, but main results and general conclusions are integrated in "General Discussion".

EXPERIMENT 1. Effects on agronomic plants, I.

Objective: To determine the effect of acid rain on the quality and quantity of growth of barley and clover growing in unfertilized soil.

Methods and Materials

Two species, subterranean clover and Briggs variety barley, were tested in a greenhouse. Seed of these species, obtained from the Davis campus of the University of California, was germinated directly in the test soil and was treated from the start with the acid sprays. The clover seed was innoculated with commercial rhizobium, as would be the case in a normal cropping situation.

Both species were grown in a Yolo soil series, which we collected from an old walnut orchard plot at the Davis campus, University of California. The plot had not been fertilized or treated with pesticide for at least two years, and was relatively undisturbed. The upper 20 cm of soil was taken to the Berkeley campus for use in the first greenhouse trial. The soil was not air-dried, but was mixed and passed through a 5-mm sieve. Thus the soil was not treated in any way that would destroy the natural microbial populations or seriously affect the physical and chemical properties.

Clay pots, 6" in diameter, were used. A plastic bag with a hole cut in the bottom, was placed in each pot, and then 1,200 g of soil was placed in each pot.

Four replications of each species-soil-treatment combination were established. A control series was also established; this was simply soil in pots, without plants, subjected to the acid spray-treatments.

Four acid spray-treatments were established, with pH 5.6, 4.0, 3.0 and 2.0. The acidities were established with a mixture of both H_2SO_4 and HNO_3 in the ratio of 2:3 based on chemical equivalents. A base-level of other ionic species was also added to each spray treatment solution; the ionic concentrations were as follows in μ equiv./liter: Mg^{2+}, 6: Ca^{2+}, 7; NH_4^+, 15; Cl^-, 15; K^+, 1.5. The acid treatment solutions were made up in 19 liter, glass containers. The base level of salts was first added, then sufficient H_2SO_4 + HNO_3 added to bring the solution to the exact pH.

The pots were sprayed with a hand-held spraying apparatus, attached to a pressurized plastic bottle filled with acid treatment solution. A piece of plastic pipe slightly smaller than the pot was placed over the plant during spraying to ensure that all the treatment solution entered the pot. Each spraying episode consisted of 250 ml per pot.

Within each pH-treatment, two to three pots were equipped with soil tensiometers, to trace moisture depletion and thus allow planning of the watering schedule. Between the acid spraying which was done approximately each week, various volumes of distilled water (usually 250 ml) was added to each pot directly to the

soil (i.e. not on the foliage), to prevent wilting. These additional irrigations were done when the soil moisture tension in the unplanted soils dropped below -0.6 bars.

Extra replicates of both clover and barley were harvested at intervals of 3 and 6 weeks, as well as at the final harvest following a total of 10 weeks growth, but only the final harvest data is presented in this report.

At harvesting, both plant tops and roots were taken. Barley heads were also segregated. The plant material was oven-dried at $65^{o}C$ in a forced-draft oven, and dry-weights were determined. Soil samples were also taken for pH measurements, and other chemical analyses. Soils were stored in plastic bags and refrigerated.

Plant material was also sampled for scanning electron microscopy (SEM) examination. Details of SEM methods are given in Appendix 1A.

Data were punched on computer cards. Summarization of data, and subsequent statistical analyses were made using the SPSS package programs, i.e. "Statistical Programs for the Social Sciences" (Nie et al, 1975), which are on file at the Computer Center, University of California, Berkeley. The main features of the experiment are summarized in Table 1.

Table 1. Main features of design of Experiment 1;
          effects on barley and clover in unfertilized
          soil.

Test species	Clover, barley
Test soil	Yolo, unfertilized
Replications	4
pH treatments	5.6, 4.0, 3.0, 2.0
Acid used	2:3 mix of H_2SO_4:HNO_3, plus base-level of other salts
Treatment period	10 weeks; sub-harvests at 3 and 6 weeks also.
Plant Harvest data	Dry weight of plant tops and roots separately; barley heads also. Nutrient analyses, particularly of tops and barley heads. Soil pH, C.E.C., and various nutrients.
Detailed analysis of leaf surfaces	Scanning electron microscopy

Results and Discussion

Means of the four replications are given in Tables 2, 3, 4, and 5 where total nutrient uptake and nutrient concentrations in plant parts, soil concentrations, dry weights of plant parts and plant water use, are given for each acid-treatment. Analyses of variance to distinguish between-treatment effects were conducted, and differences between means (at the 5% level of probability) were determined. Means that are statistically different by Duncan's multiple-range test are also identified in Tables 2, 3, 4 and 5. For convenience, the main results are summarized as follows under the subheadings: 1. soil, 2. clover, 3. barley, 4. water use, and 5. tissue damage. Ions analysed, but not mentioned below, did not differ between treatments or else differences were so mixed that trends were not discernable.

1. Soil: Soil from the control pots without plants, and soils in which the barley or clover were growing, were analyzed separately.

(a) soil in the control pots (Table 2): input acid-treatment solutions of pH 2.0 generally increased the amount of available Mn, Fe, Mg and NO_3. These increases in the pH 2.0 treatment were also accompanied by a slight decrease in Ca, and a lowering of the soil pH (Fig. 3).

Al and NH_4 appeared to be highest in the pH 5.6 treatment. In the case of NH_4, nitrification may have been retarded in the lower pH treatments. However, an assay of the rate of nitrification at harvest did not reveal any significant differences between treatments.

(b) <u>soil planted with clover (Table 3)</u>: The following ions showed significant decreases at treatment pH 2.0 and/or pH 3.0: Al, NO_3, K. Soil pH was also significantly lower with inputs of pH 2.0 and 3.0 (Fig. 3).

Somewhat unusual was the higher Cu at pH 5.6, and the lower Al at pH 2.0 (mentioned earlier). NH_4 increased with decreasing pH treatment.

(c) <u>soil planted with barley (Table 4)</u>:

The statistically significant results were: decreases in soil pH (Fig. 3) and K with decreasing pH-treatment, and greater Fe, Al and NH_4 at pH 5.6. Fe was also high in pH 2.0 treatment.

Table 2. Chemical characteristics of unplanted soil following acid treatments; Experiment 1.

Characteristic[1]	pH treatment[2]			
	5.6	4.0	3.0	2.0
Na	0.13 a	0.14 a	0.14 a	0.15 a
K	0.78 a	0.73 a	0.76 a	0.79 a
Ca	8.16 a	8.10 a,b	8.11 a,b	7.61 a
Mg	10.04 a	9.91 a	9.91 a	12.18 b
Mn	1.20 b	0.70 a	0.82 a	1.98 c
Cu	0.80 b,c	0.60 a	0.69 a,b	0.88 c
Fe	2.05 a	1.49 a	2.48 a	7.78 b
Zn	1.12 b	0.75 a	0.85 a,b	1.05 a,b
Al	0.05 b	0.03 a,b	0.02 a	0.03 a
NO_3	10.76 a	6.32 a	17.48 a	281.98 b
NH_4	1.70 a,b	2.03 b	1.50 a	1.40 a
Total-N	837.5 a	825.0 a	838.8 a	815.0 a
pH	7.10 a	a	7.43 a	6.55 a

[1]Units: Na, K, Ca, Mg are meq/100g soil; Mn, Cu, Fe, Zn, Al, NO_3, NH_4, Total-N are µg/g soil.

[2]Different letters indicate differences between means at 5%; Duncan's multiple-range test.

2. Clover (Table 3):

The following ions in the shoots decreased in concentration with increasing acidity of treatment solution, although significant differences were exhibited only for the pH 2.0 treatment in most cases: Na, Ca, Mg, Mn, Zn. These lower concentrations were largely a product of the greater plant size in the pH 2.0 and 3.0 treatments, due to a "fertilizer effect" by the added N and S in these acid treatment solutions.

Concentrations of P, S, and N in shoots, and N in roots increased with the pH 2.0 treatment.

Although there were significant differences shown for K, Cu and Fe, responses were mixed, and trends related to pH treatments were diffuse.

The main response to acid inputs, however, was the increased growth with increasing acidity of input. This was largely a response to added N and S by the treatment solutions, i.e. a "fertilizer effect" (Fig. 4). Shoot dry weights and total (roots and shoots) dry weight and total N in plant tops were significantly greater in pH 3.0 and 2.0 treatments (Fig. 5), and total (roots and shoots) nitrogen was significantly higher in pH 2.0 treatment (Table 3).

The larger plants in pH 3.0 and 2.0 resulted in greater total uptake of most elements in the more acid treatments, than at pH 5.6 or 4.0. Specifically, there was significantly greater uptake at pH 3.0 and/or 2.0 for the following elements in shoots of clover:

Na, K, Ca, Mg, Mn, Cu, Fe, Zn, Al, P, S, N. Root-N also showed greater uptake at pH 3.0 and 2.0 treatments.

Caution must be used in interpretation of the N and S results, as both N and S were added in increasing amounts with the treatments (Fig. 4). These N and S additions, then, may have been absorbed directly by the foliage or may have been impacted on the foliage surface, rather than being deposited on the soil and subsequently taken up by roots.

Although the plants were larger and greener in the pH 2.0 and 3.0 treatments, the leaves had necrotic, white spots from acid droplets; these visual symptoms of acidic damage were not observed in the pH 4.0 or 5.6 treatments.

Table 3. Chemical characteristics of soil planted with clover, and of clover plant parts following acid treatment; Experiment 1.

Characteristic[1]	pH treatment[2]			
	5.6	4.0	3.0	2.0
Clover Soil:				
Na	0.11	--	--	0.13
K	0.55	--	--	0.36
Ca	8.0	--	--	7.5
Mg	9.8	--	--	10.0
Mn	3.36 a	3.51 a	2.59 a	3.29 a
Cu	1.26 b	0.91 a	0.80 a	0.87 a
Fe	4.37 a	4.63 a	3.39 a	10.29 b
Zn	1.25 a	1.46 a	3.12 a	1.95 a
Al	0.02 a	0.02 a	0.03 a	0.10 b
NO_3	1.70 a	1.84 a	11.02 b	16.83 c
NH_4	1.27 a	2.26 a,b	2.56 b	4.57 c
Total N	843 a	870 a,b	925 c	881 b
pH	6.65 b	6.63 b	6.05 a	6.05 a

[1]Units: For soil: Na, K, Ca, Mg are meq/100g soil; Mn, Cu, Fe, Zn, Al, NO_3, NH_4, Total-N are µg/g soil. For plants: all concentrations are ppm; mass of nutrients is concentration X dry weight in grams; weights are grams per pot.

[2]Different letters indicate differences between means at 5%; Duncan's multiple-range test.

Table 3 (continued)

Characteristic	pH treatment			
	5.6	4.0	3.0	2.0
Clover Shoot concentration:				
Na	626 b	613 b	248 a	367 a
K	24,641 b	22,873 b	19,266 a	24,059 b
Ca	16,830 b	16,929 b	12,333 a	13,282 a
Mg	10,272 c	10,272 c	7,833 a	8,911 b
Mn	106.0 a	101.5 a	116.0 a	92.0
Cu	15.8 b	6.5 a	14.3 a,b	22.7 b
Fe	764 b	216 a	572 a,b	297 a
Zn	69.5 b	59.8 b	46.8 a	47.2 a
Al	291 a	345 a	402 a	181 a
P	3,050 a	3,162 a	3,287 a	4,212 b
S	430 a	344 a	438 a	4,064 b
N	13,980 a	13,233 a	16,488 b	26,748 b
Clover Root concentration:				
N	18,330 a	17,795 a	15,861 a	23,505 b

Table 3 (continued):

Characteristic	pH treatment			
	5.6	4.0	3.0	2.0
Mass in clover shoot:				
Na	4,839 a	4,302 a	5,633 a	7,544 b
K	184,359 b	161,119 a	438,980 c	489,779 d
Ca	125,900 a	119,226 a	280,108 b	273,553 b
Mg	77,330 a	72,317 a	178,086 b	183,502 b
Mn	793 a	716 a	2,638 b	1,958
Cu	119 a	46 a	325 b	463 c
Fe	5,900 b	1,521 a	13,190 c	6,102 b
Zn	421 a	520 b	1,063 d	973 c
Al	2,219 a	2,456 a	9,354 b	3,765 a
P	23,143 a	22,247 a	74,862 b	86,817 c
S	3,361 a	2,433 a	9,964 a	84,118 b
N	106,514 a	93,069 a	376,041 b	551,333 c
Mass in clover root:				
N	43,736 a,b	29,890 a	54,287 b	61,863 b
Mass in clover root + shoot:				
N	150,250	122,959	430,328	613,196
Shoot weight	7.56 a	7.04 a	22.81 c	20.62 b
Root weight	2.44 a,b	1.68 a	3.50 b	2.64 a,b
Shoot + root weight	10.0 a	8.7 a	26.3 c	23.3 b

EFFECTS OF TREATMENTS ON BULK SOIL pH
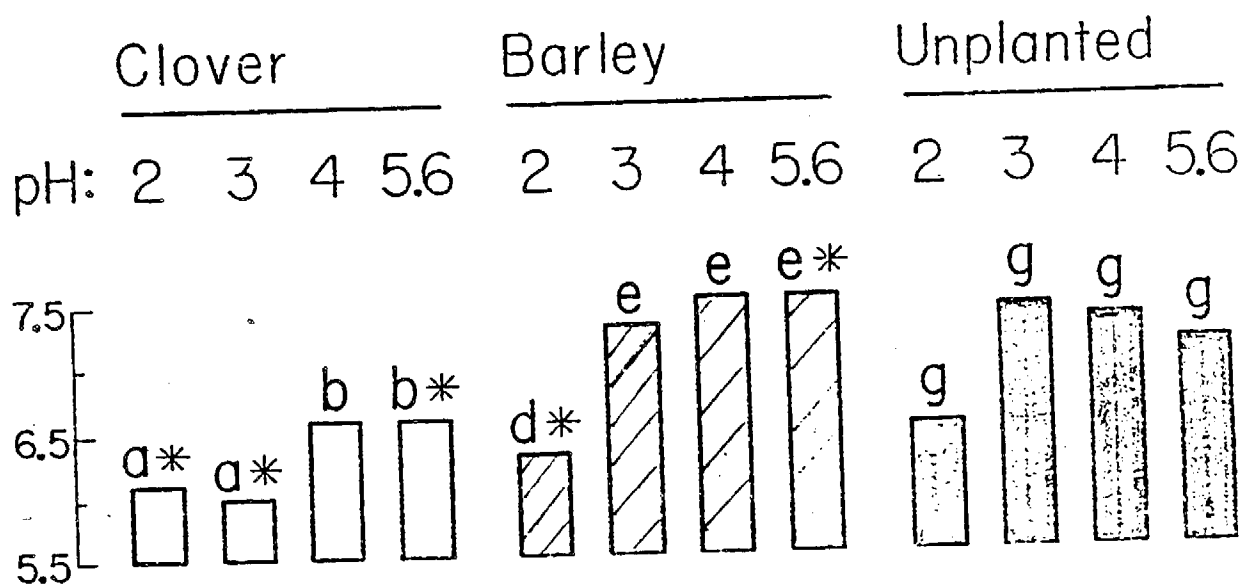
Fig. 3. Effects of acid rain treatments on the pH of soil planted with barley, clover, and unplanted. Experiment 1. (Different letters indicate differences between treatment means within a species at 5%; Duncan's multiple-range test. Paired t-tests were also conducted to distinguish differences between the pH of unplanted soil and the soil planted with barley or clover; significant differences at the 5% level between the unplanted and planted soil for each respective pH-treatment, are indicated by asterisks.)

Total N Input as HNO₃

Total N Input as HNO_3

Total S Input as H₂SO₄

Total S Input as H_2SO_4
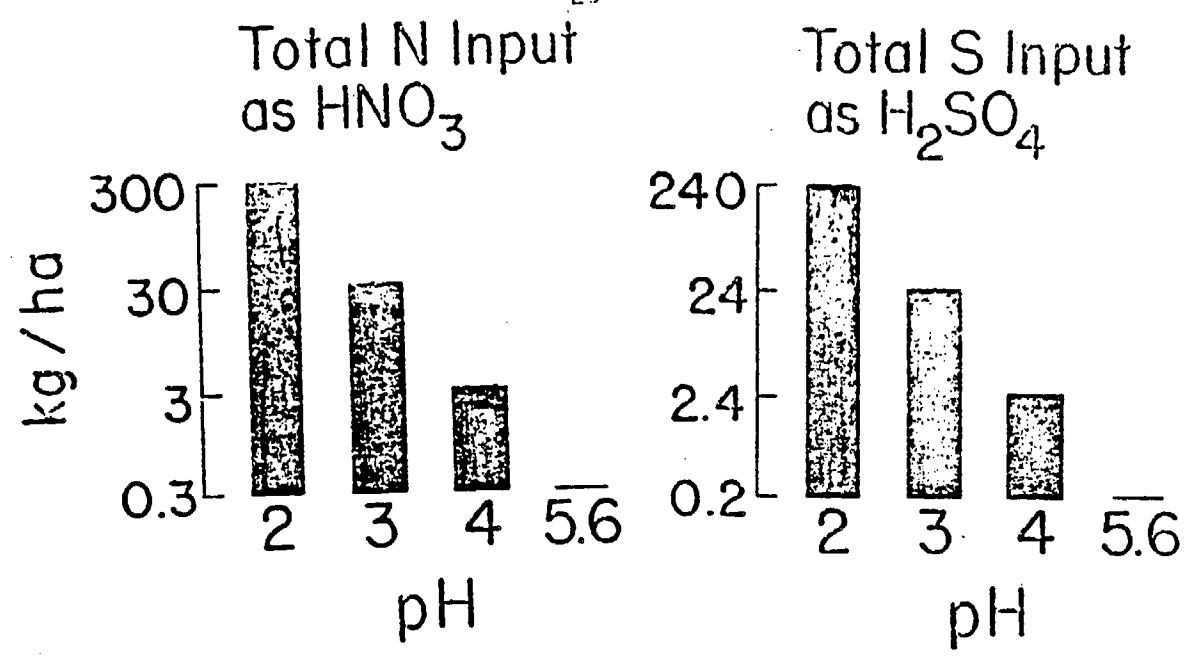
Fig. 4. Inputs of nitrogen and sulfur in the acid rain treatments. Experiment 1.
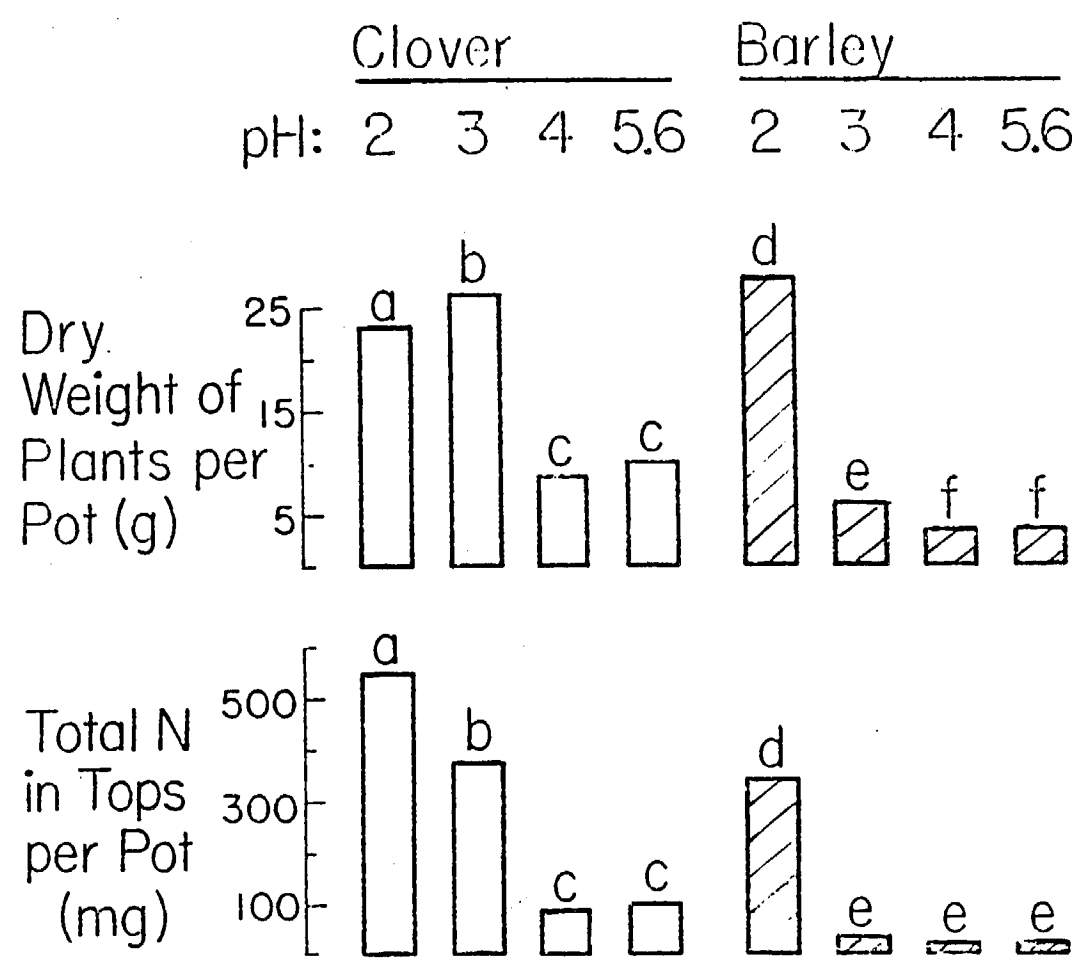
Fig. 5. Dry weight and nitrogen content of clover and barley grown under various acid rain treatments. Experiment 1. (Different letters indicate differences between means at 5%; Duncan's multiple-range test.)

3. <u>Barley (Table 4)</u>:

Similar results were obtained for barley. The main effect (as was the case for clover) was a "fertilizer effect" by N and S additions (Fig. 4), in the pH 3.0 and 2.0 treatments, which resulted in larger plants. Shoots, roots, and heads, either considered separately or together, were greater in dry weight in the pH 2.0 treatment, and in most cases pH 3.0 treatment also (e.g. Fig 5, shoots, and Table 4).

Concentration in shoots were significantly lower in the more-acid treatments (primarily pH 2.0) for K, Ca, Mg, Mn, and to some extent, Zn. Concentrations were significantly higher in shoots for N (Fig. 5).

In barley heads, concentrations were higher in the more-acid treatments for K, Mn, Cu, Fe, S and N. Zinc showed a mixed response at the different pH treatments. Total uptake in barley heads was greater in the pH 2.0 treatment, for all nutrients analyzed (Table 4).

In nearly all cases, there was a significant increase in the plant uptake of nutrients in the pH 2.0 treatment; specifically for the following: Na, K, Ca, Mg, Mn, Cu, Fe, Zn, Al, P, S, N (Table 4). These greater amounts at pH 2.0 were essentially a product of the larger plants, due to the "fertilizer effect" (Fig. 4).

In the pH 2.0 treatment, white or brown spots and lesions from acid droplets were observed on leaves, although the general health and green coloration was good.

Table 4. Chemical characteristics of soil planted with barley, and of barley plant parts following acid treatments. Experiment 1.

Characteristic[1]	pH treatment[2]			
	5.6	4.0	3.0	2.0
Barley soil:				
Na	0.12 a	0.12 a	0.14 a	0.10 a
K	0.64 a	0.64 b	0.57 b	0.33 a
Ca	8.39 a	8.33 a	8.17 a	8.32 a
Mg	10.23 b	10.18 a,b	9.93 a	10.40 b
Mn	2.91 b	2.22 a,b	1.32 a	2.89 b
Cu	0.82 b	0.67 a,b	0.57 a	0.79 b
Fe	6.77 b,c	3.40 a,b	1.68 a	8.80 c
Zn	2.15 a	2.33 a	1.04 a	0.94 a
Al	0.087 b	0.015 a	0.035 a	0.023 a
NO_3	2.34 a	2.13 a	3.86 a	1.23 a
NH_4	2.20 b	1.30 a	1.23 a	1.37 a
Total N	841 a,b	849 a,b	816 a	856 a
pH	7.57 c	7.48 c	7.33 b	6.28 a
Barley Shoot concentration:				
Na	560 a	730 b	684 b	632 a,b
K	34,772 b	35,108 b	35,453 b	31,286 a
Ca	3,783 b,c	3,922 c	3,409 a,b	3,004 a
Mg	5,990	6,304 b	5,493 b	4,176 a
Mn	60.3 c	54.2 b,c	43.7 a,b	37.0 a
Cu	25.0 a	18.7 a	24.5 a	29.3 a

Table 4 (continued)

Characteristic	pH treatment			
	5.6	4.0	3.0	2.0
Barley Shoot concentration (cont.)				
Fe	55.0 a	79.8 a	80.5 a	92.8 a
Zn	38.0 b	35.8 a,b	30.5 a	35.5 a,b
Al	37.3 a	43.7 a	49.0 a	133.3 a
P	9,017 c	9,825 c	6,563 b	3,963 a
S	1,023 a	1,029 a	2,606 a	2,419 a
N	5,130 a	5,905 a	6,152 a	13,104 b
Barley Root concentration:				
N	7,602 a	7,977 a	7,265 a	9,136 a
Barley Head concentration:				
Na	105.7 a	56.8 a	64.5 a	65.5 a
K	5,902 a	6,894 a,b	8,497 b,c	10,172 c
Ca	--	--	--	--
Mg	1,991 b	2,055 b	1,793 a	1,993 b
Mn	22.0 a	18.3 a	17.8 a	27.3 b
Cu	15.5 a,b	8.0 a	9.0 a	22.5 b
Fe	46.0 a,b	38.0 a	34.5 a	54.0 b
Zn	71.0 c	54.8 a,b	46.8 a	66.5 b,c
Al	4.0 a	5.5 a	4.5 a	12.0 a
P	5,200 a	4,900 a	4,675 a	4,725 a
S	10,858 a	12,621 a	12,003 a	17,576 b
N	17,916 a	15,782 a	16,040 a	19,802 b

Table 4 (continued)

Characteristic	pH treatment			
	5.6	4.0	3.0	2.0
Mass in Barley Shoots:				
Na	1,024 a	1,287 a	1,900.4 a	11,743 b
K	65,112 a	62,947 a	98,535 a	579,954 b
Ca	7,026 a	7,043 a	9,577 a	55,649 b
Mg	11,180 a	11,280 a	15,196 b	.77,397 c
Mn	111 a	98 a	122 a	687 b
Cu	44 a	32 a	65 a	539 b
Fe	100 a	137 a	230 a	1,718 b
Zn	70 a	64 a	86 a	660 b
Al	69 a	75 a	146 a	2,435 a
P	16,679 a	17,223 a	18,011 a	73,624 b
S	1,890 a	1,836 a	7,155 a	44,936 b
N	9,294 a	10,220 a	17,079 a	243,598 b
Mass in Barley Roots:				
N	6,194 a	6,664 a	13,101 a	45,414 b
Mass in Barley Heads:				
Na	47.8 a	4,16 a	72.1 a	318,2 b
K	4,136 a	4,898 a	9,526 a	47,268 b
Ca	--	--	--	--
Mg	1,438 a	1,493 a	2,038 a	9,543 b
Mn	14.4 a	13,3 a	20.4 a	129.5 b
Cu	8.97 a	5,52 a	10.0 a	101.8 b
Fe	27,8 a	27,1 a	39.0 a	252.2 b

Table 4 (continued)

Characteristic	pH treatment			
	5.6	4.0	3.0	2.0
Barley Shoot weight	1.85 a	1.78 a	2.82 b	18.55 c
Barley Root weight	0.87 a	0.88 a	1.94 a	4.76 a
Barley Head weight	0.71 a	0.73 a	1.14 a	4.78 b
Barley S + R + H weight	3.43 a	3.38 a	5.90 b	28.10 c

Table 4 (continued)

Characteristic	pH treatment			
	5.6	4.0	3.0	2.0
Mass in Barley Heads:				
Zn	47.6 a	40.5 a	52.1 a	314.2 b
Al	3.76 a	3.95 a	4.76 a	62.0 b
P	3,581 a	3,592 a	5,255 a	22,619 b
S	7,556 a	8,969 a	13,880 a	85,683 b
N	11,198 a	11,566 a	18,129 a	95,712 b
Mass in Shoots + Heads:				
Na	1,071 a	1,328 a	1,973 b	12,061 b
K	69,248 a	67,845 a	108,062 a	627,221 b
Ca	11,181 a	11,280 a	15,197 b	77,397 c
Mg	1,550 a	1,592 a	2,160 a	10,231 b
Mn	57.0 a	45.1 a	81.8 a	681.7 b
Cu	77.0 a	86.6 a	156.1 a	2,536.7 a
Fe	127.6 a	164.8 a	269.1 a	1,969.8 b
Zn	117.6 a	104.5 a	137.7 a	974.3 b
Al	72.9 a	79.1 a	150.8 a	2,496.9 b
P	20,261 a	20,815 a	23,267 a	96,244 b
S	9,446 a	10,806 a	21,035 a	130,619 b
N	21,213 a	21,787 a	35,208 b	339,309 c
Mass in total barley plant:				
N	27,407 a	28,451 a	48,309 b	384,723 c

[1]Units: For soil: Na, K, Ca, Mg are meq/100g soil; Mn, Cu, Fe, Zn, Al, NO_3, NH_4, Total-N are μg/g soil. For plants: all concentrations are ppm; mass of nutrients is concentration X dry weight in grams; weights are grams per pot.

[2]Different letters indicate differences between means at 5%; Duncan's multiple-range test.

4. <u>Water Use (Table 5 and Fig. 6)</u>

Water volumes added throughout the pot-trial were recorded. Water-use included both transpired water and water evaporated from the soil surface. There was a significant correlation between cumulative water use (for the total duration of the experiment), and plant dry weights at the final harvest. Thus water use is a reasonably good measure of total productivity throughout the experimental period (Fig. 6). These figures show greater total water-use for plants in the pH 2.0 treatment in the case of barley, and pH 3.0 treatment for clover. However, when water-use is expressed on a per gram dry weight basis, different patterns emerge that illustrate the "efficiency" of water use. For both species the water-use per gram of plant was greatest in the higher pH treatments and least in the lower pH treatments (Table 5). Water was more efficiently used by the larger plants in the more-acid treatments, although the larger plants did in fact use more water.

Table 5. Water-use by barley and clover grown under various acid rain treatments. Experiment 1.

Water use (liters)	pH treatment[1]			
	5.6	4.0	3.0	2.0
Barley:				
Total	6,210	6,888	6,382	11,617
per gm. shoot	3,391 a	3,926 a	2,346 b	627 c
per gm. root	8,045 a,b	8,417 a	3,946 b,c	3,078 c
Clover:				
Total	10,278	10,434	15,984	12,333
per gm. shoot	1,375 b	1,485 b	702 a	599 a
per gm. root	4,304 a	4,894 a	5,108 a	6,388 a

[1]Different letters indicate differences between means at 5%; Duncan's multiple-range test.
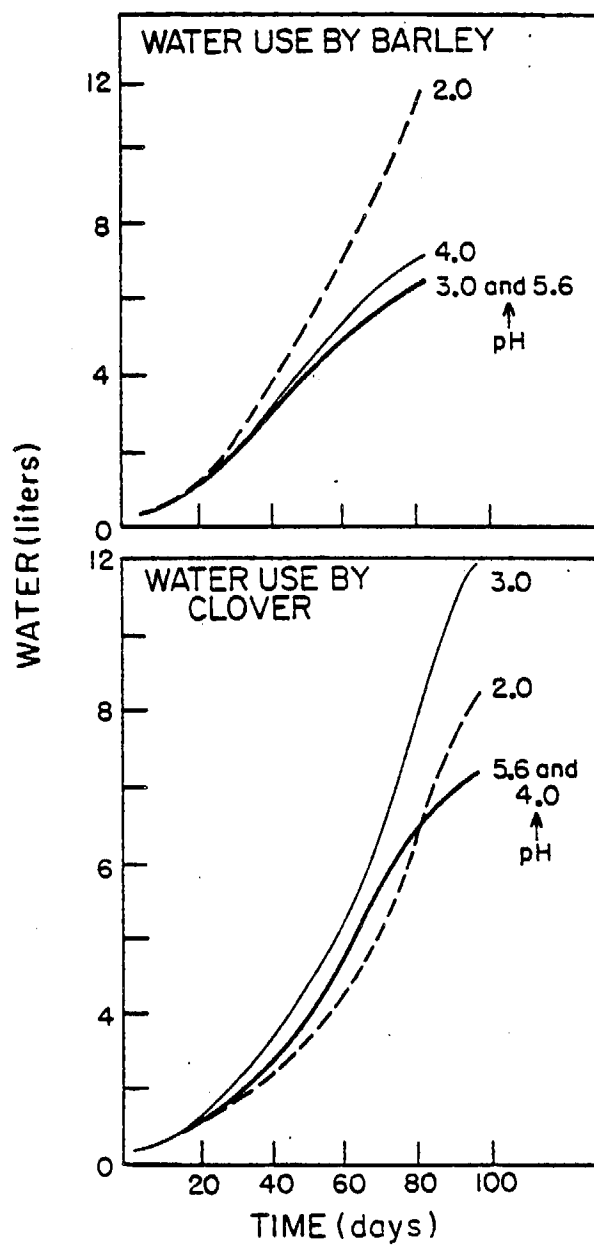
Fig. 6. Water use by barley and clover grown under various acid rain treatments. Experiment 1.

5. <u>Tissue damage (Fig. 7)</u>

Scanning electron microscopy (S.E.M.) of leaf samples of both barley and clover revealed differences between extreme pH treatments of 5.6 and 2.0 (samples from intermediate pH treatments were not observed using S.E.M. techniques). In samples from the pH 2.0 treatment, leaf-surface waxes were removed or aggregated, and evidence of cuticular damage can be seen. Although the plants appeared to be otherwise healthy in the low-pH treatments, leaf-surface damage may lead to increased transpiration, and greater susceptibility to insect and fungal attack. However, these phenomena were not observed or specifically studied in this experiment.
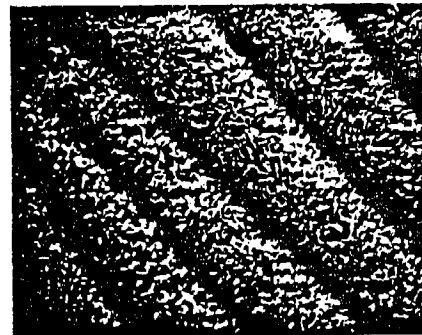
Fig. 7. Scanning electron micrographs of leaf-surfaces of clover and barley, grown under acid rain treatments, pH 2.0 and 5.6. Experiment 1.

EXPERIMENT 2.   Effects on agronomic plants, II.

Objective: To determine the effect of acid rain on the quality and quantity of growth of barley, clover, cabbage, sugar beet and soft chess growing in both unfertilized and fertilized soil.

Methods and Materials:

Treatment of the soil-plant systems were carried out in a series of four specially constructed "rooms" within a lathhouse, in which specific acid-rain sprays are maintained. Each room was 8' x 8' x 10' high, made of a wood frame covered with polyethylene to isolate each treatment, one from another, and to shield the treated plants from natural rain inputs. Four separate spraying systems (reservoirs of acidic inputs, pumps, etc.) provided simulated acid rain to each of the four rooms. All parts of the spraying system were constructed of plastic, stainless steel, or glass to prevent corrosion (and consequent contamination) of the acidic treatment solutions.

Bulk quantities of acidic treatment solutions were made up in 30 gallon plastic containers (i.e. garbage cans). The four pH treatments were 5.6, 4.0, 3.0 and 2.0, using a 2:3 mixture of H_2SO_4 : HNO_3 in the appropriate quantities for each treatment. The pH of the resulting bulk solutions were checked with a pH-meter; pH-treatments 2.0, 3.0 and 4.0 had measured pHs of $\pm$ 0.1, and the pH 5.6 treatment, $\pm$ 0.3 (this solution was obviously less buffered). A base-level of other ions were also added to the acidic treatment solutions, in the following concentrations in μ equiv./liter: Mg^{2+}, 6; Ca^{2+}, 7; NH_4^+ 14; Na^+, 15; Cl^-, 15; K^+, 1.5.

Spray nozzles (4 in each treatment room) deliver raindrops of an average size conformable to that of normal rainfall; the nozzles were mounted on a moveable beam that was manually rotated an eighth turn at intervals during each twenty-minute spray-period; this improved uniformity of the spray distribution. The distribution precision (coefficient of variation) was 30% when all rooms were considered together, and about 20% within each room, which compares favorably with similar studies (e.g. Shriner et al, 1977).

Total water input over the 10 weeks of treatment was equal to rianfall of 5.2 $\pm$ 1.7", this being equivalent to about 16 $\pm$ 5" for a six-month rainy season, which is quite typical for many parts of California.

Two soil series, a Yolo and a Shaver, were used in this pot trial. The Yolo was collected in the same location, as described in Experiment #1, from near the Davis campus. The Shaver soil, a typical mid-elevation, granitic, Sierra Nevada soil, was collected near Dinkey Creek, Fresno County, in a typical mixed-conifer forest. The litter layer was first removed, and the soil collected from the A-horizon. Both soils were not air-dried, but were passed through a 2 mm sieve. For the Yolo soil, 1,800 g per pot and for the Shaver soil, 1,400 g per pot were used. Barley, clover, cabbage and sugar beet were grown in the Yolo soil, and soft chess grown in the Shaver soil. Seed was germinated directly in the pots and watered with distilled water during germination. The final numbers of seedlings per pot, following thinning, were as follows: barley 3, clover 3, soft chess 16, cabbage 1, sugar beet 1.

The plant-species-soil combinations were also completely replicated, but in this case soil fertilizers were also added; nitrogen was added at the rate of 0.16 g per pot (equivalent to 200 lbs/acre of N) as NH_4NO_3, and sulfur at the rate of 0.056g per pot (equivalent to 70 lbs/acre of S) as $CaSO_4$ $2H_2O$.

Data were punched on computer cards. Summarization of data, and subsequent statistical analyses were made using the SPSS package programs, i.e. "Statistical Programs for the Social Sciences" (Nie et al, 1975) which are on file at the Computer Center, University of California, Berkeley.

The main features of the experiment are summarized in Table 6.

Table 6. Main features of design of Experiment 2: effects
on various agronomic species in both fertilized
and unfertilized soil.

Test species	Clover, barley, cabbage, sugar beet, soft chess.
Test soils	Yolo, for all species except soft-chess. Shaver, for soft-chess. Both fertilized with N and S, and unfertilized.
Fertilizer treatments	N as NH_4NO_3 at 200 lbs/ac. S as $CaSO_4 \cdot 2H_2O$ at 70 lbs/ac.
pH treatments	5.6, 4.0, 3.0, 2.0
Replication	6
Acid used	2:3 mix of H_2SO_4 : HNO_3, plus base-level of other salts.

Treatment and growth periods (weeks)

Species	Acid Treatment	Seed to Harvest
Barley	9	11
Clover	9	12
Cabbage	9	12
Sugar beet	10	12
Soft chess	6	10
Control soil, Yolo (unplanted)	10	14

Plant harvest data	Dry weights of plant tops and roots separately. Nitrogen analysis of plant shoots.
Soil data	Surface soil, as well as bulk-soil sampled for pH.

Results and Discussion (Table 7, 8 and 9, and Figures 8 and 9)

In unfertilized Yolo soil, plant tops were greatest at pH 2.0 for barley, but roots maximized at pH 3.0 treatment; sugar beet and clover also showed maximum shoot growth at pH 3.0 (Fig. 8 and Table 7). Cabbage had maximum growth in at pH 2. These increased growth in low pH treatments are attributed to the "fertilizer effect" of the added N and S in the input acid-solutions, as was documented in experiment 1 earlier (Fig. 4 and 5).

In the unfertilized Shaver soil, soft chess showed maximum growth at pH 2. The relative increase in growth in this treatment was greater than that for the other species growing in the Yolo soil, as the Shaver soil had less available nutrients, and any "fertilizer effect" would therefore be more pronounced.

Fertilization of the soil increased plant growth over unfertilized conditions, for all plant species and over pH treatments (Fig. 8 and Table 8). Soft chess in Shaver soil had no significant differences between shoot weight at the different pH treatments, illustrating the fact that sufficient soil fertilizers were added to overcome any deficiencies; however, root growth did maximize in pH 3.0 treatment.

For the species in the Yolo soil, however, there were still growth responses to the pH treatments even when the soil had been fertilized (Fig. 8); barley, clover and sugar beet maximized at pH 3.0 and cabbage at pH 2.0. (The original pH of the Yolo soil was about 7.5) (Fig. 9A), whereas the Shaver with soft chess had an initial pH of about 6.5 (Fig. 9B). The lowering of the soil pH in the Yolo soil may have made other nutrients (such as K^+, Mg^{2+}, Ca^{2+}) more available, thus increasing growth from the higher pH (3.0 or 2.0, depending on the species). In the Yolo soil in the pH 2.0 treatment, the soil pH was significantly lower for all species both for the

upper and lower soil in the pots; for surface soil, it dropped to pH 6.2 in barley, 6.5 in clover, 6.0 for cabbage, and 5.2 for sugar beet. For unplanted Yolo soil, surface soil pH dropped to 6.5 in the pH 2.0 treatment, but only to 7.0 at the lower soil depths (Fig. 9A).

In the Shaver soil supporting soft chess, the drop in soil pH at the pH 2 treatment level was very marked, i.e. from 6.6 to 5.3 in the upper soil (Fig. 9B).

The fertilizer-salt also reduced soil pH (Fig. 8), probably because of the acidifying effect of the NH_4NO_3 used.

Two-way analyses of variance were also carried out to distinguish interactions between applied treatments in this experiment. In Table 9, results of these statistical analyses are indicated by the significance of the F-ratio; values greater than 0.05 are considered significant. In nearly all cases, treatment pH significantly affected plant weights, except for clover roots (Table 9). Addition of soil fertilizers also had some significant effects, although root weights were unaffected in clover, barley, cabbage and sugar beet growing in Yolo soil, and shoot weight of cabbage was also unaffected (Table 9). Interaction between pH treatments and fertilization was not very apparent for the species growing in the Yolo soil, but did effect both the root and shoot growth of soft chess growing in the Shaver soil (Table 9).

The experimental results as a whole indicate that the simulated acid rain can enhance growth of plants, not only by providing needed N and S in unfertilized soil, but by increasing the availability of additional ionic species in soil that may be deficient. However, in many cases, decreased growth occurred from the pH 3 to the pH 2 treatment, indicating that excessive

acid inputs are detrimental to plant growth in soils adequately supplied with native nutrients or added fertilizers.

Plant species respond differently to acid inputs. Sugar beet was particularly sensitive, with maximum growth at the pH 3 treatment; plants in both pH 3 and pH 2 treatments had necrotic spots on leaves and were generally unhealthy in appearance. The other species, however, showed little or no visual symptoms of sensitivity to acidity, even in the pH 2 treatment.

Table 7. Soil pH at upper and lower depths, and plant productivity for barley, clover, cabbage and sugar beet in Yolo soil, and soft chess in Shaver soil. All soils were unfertilized. Experiment 2.

Characteristic[1]	pH Treatment[2]			
	5.6	4.0	3.0	2.0
Barley, Yolo Soil:				
upper pH	7.52b	7.58b	7.35b	6.22a
lower pH	7.67b	7.68b	7.60b	7.42a
Shoot weight	2.72a	2.75a	3.71b	5.18c
Root weight	0.95a	1.09a, b	1.98c	1.47b
Total Plant Weight	3.67a	3.84a	5.68b	6.66c
Clover, Yolo Soil:				
upper pH	7.58c	7.35c	7.28b	6.47a
lower pH	7.39b	7.33a, b	7.37b	7.20a
Shoot weight	4.43a	4.74a, b	5.40b	5.00a, b
Root weight	0.53a	0.65a	0.63a	0.57a
Total Plant Weight (incl. shoot "bases")	5.10a	5.68a, b	6.48b	5.86a, b
Cabbage, Yolo Soil:				
upper pH	7.34b	7.35b	7.45b	5.97a
lower pH	7.51b	7.45b	7.52b	7.23a
Shoot weight	2.10a	2.23a, b	3.50b,c	4.22c
Root weight	0.22a	0.13a	0.45b	0.31a, b
Total Plant Weight	2.32a	2.36a	3.95b	4.53b
Sugar beet, Yolo Soil:				
upper pH	7.36b	7.32b	7.35b	5.20a
lower pH	7.32a, b	7.28a, b	7.38b	7.18a
Shoot weight	0.90a	0.97a	1.97b	1.34a, b
Root weight	0.12a	0.21a	0.65b	0.14a
Total Plant Weight	1.02a	1.18a	2.62b	1.48a
Unplanted Yolo Soil:				
upper pH	7.37b	7.32b	7.33b	6.52a
lower pH	7.32b	7.25b	7.33b	7.00a
Soft Chess, Shaver Soil:				
upper pH	6.63c	6.60c	6.20b	5.28a
lower pH	6.60a	6.60a	6.60a	6.47b
Shoot weight	1.26a	1.42a	1.61a	3.13b
Root Weight	2.01a, b	1.70a	2.15b	2.08a, b
Total Plant Weight	3.27a	3.12a	3.76a	5.21b

[1]Plant weights are grams per pot

[2]Different letters indicate differences between means at 5%; Duncan's multiple-range test.

Table 8. Soil pH at upper and lower depths, and plant productivity for barley, clover, cabbage and sugar beet in Yolo soil, and soft chess in Shaver soil. <u>All soils were fertilized</u> with N as NH_4NO_3 at the rate of 200 lbs/ac, and S as $CaSO_4.2H_2O$ at 70 lbs/ac. Experiment 2.[2]

Characteristic[1]	pH Treatment[2]			
	5.6	4.0	3.0	2.0
Barley, Yolo Soil:				
upper pH	7.33c	7.30c	6.83b	6.08a
lower pH	7.48b	7.47b	7.25a	7.17a
shoot weight	4.56a	4.75a, b	7.45c	5.72b
root weight	1.27a	1.01a	2.37b	1.33a
Total Plant Weight	5.83a	5.75a	9.82b	7.04a
Clover, Yolo Soil:				
upper pH	7.42b	7.42b	6.78a	6.37a
lower pH	7.27a	7.22a, b	7.14b	7.20a, b
shoot weight	5.03a	5.28a	6.43a	5.73a
root weight	0.55a	0.63a	0.71a	0.54a
Total Plan Weight (incl. shoot "bases")	5.81a	6.24a, b	7.93b	6.64a, b
Cabbage, Yolo Soil:				
upper pH	7.40c	7.32b, c	7.22b	5.90a
lower pH	7.25b	7.23b	7.30b	6.92a
shoot weight	3.01a	1.77a	4.77b	5.18b
root weight	0.33a	0.15a	0.36a	0.37a
Total Plant Weight	3.34a, b	1.95a	5.13b, c	5.54c
Sugar Beet, Yolo Soil:				
upper pH	7.16b	7.10b	7.06b	5.96a
lower pH	7.06b	7.16b	7.06b	6.86a
shoot weight	1.88a, b	1.44a	2.88b	0.92a
root weight	0.34a, b	0.31a, b	0.60b	0.10a
Total Plant Weight	2.22a, b	1.75a	3.48b	1.22a
Unplanted, Yolo Soil:				
upper pH	7.35b	7.38b	7.40b	6.41a
lower pH	7.01b, c	6.93a, b	7.10c	6.85a
Soft Chess, Shaver Soil:				
upper pH	6.42c	6.38c	6.17b	5.12a
lower pH	6.28a	6.34a, b	6.37b	6.37b
shoot weight	4.08a	4.13a	4.30a	4.51a
root weight	2.11a, b	2.36b	3.67c	1.51a
Total Plant Weight	6.06a	6.49a	8.15b	6.01a

[1] Plant weights are grams per pot.

[2] Different letters indicate differences between means at 5%; Duncan's multiple-range test.

Table 9. Results of two-way analysis of variance
(between treatment pH and fertilization)
as shown by the significance of the F ratio,
for upper and lower soil pH and plant produc-
tivity for barley, clover, cabbage and sugar
beet in Yolo soil, and soft chess in Shaver
soil. Experiment 2.

| Characteristic | Significance of F | | |
	Treatment pH	Fertilization	Interaction
Barley, Yolo Soil:			
upper pH	0.001	0.001	0.054
lower pH	0.001	0.001	0.323
shoot weight	0.001	0.001	0.001
root weight	0.001	0.323	0.285
Total Plant Weight	0.001	0.001	0.001
Clover, Yolo Soil:			
upper pH	0.001	0.002	0.177
lower pH	0.017	0.001	0.145
shoot weight	0.013	0.013	0.915
root weight	0.354	0.692	0.930
Total Plant Weight (incl. shoot "bases")	0.004	0.017	0.798
Cabbage, Yolo Soil:			
upper pH	0.001	0.047	0.039
lower pH	0.001	0.001	0.573
shoot weight	0.001	0.099	0.399
root weight	0.004	0.578	0.500
Total Plant Weight	0.001	0.085	0.461
Sugar Beet, Yolo Soil:			
upper pH	0.001	0.997	0.084
lower pH	0.001	0.001	0.057
shoot weight	0.001	0.030	0.120
root weight	0.001	0.342	0.454
Total Plant Weight	0.001	0.031	0.339
Unplanted Yolo Soil:			
upper pH	0.001	0.913	0.361
lower pH	0.001	0.001	0.224
Soft Chess, Shaver Soil:			
upper pH	0.001	0.001	0.182
lower pH	0.015	0.001	0.001
shoot weight	0.001	0.001	0.001
root weight	0.001	0.016	0.001
Total Plant Weight	0.001	0.001	0.001
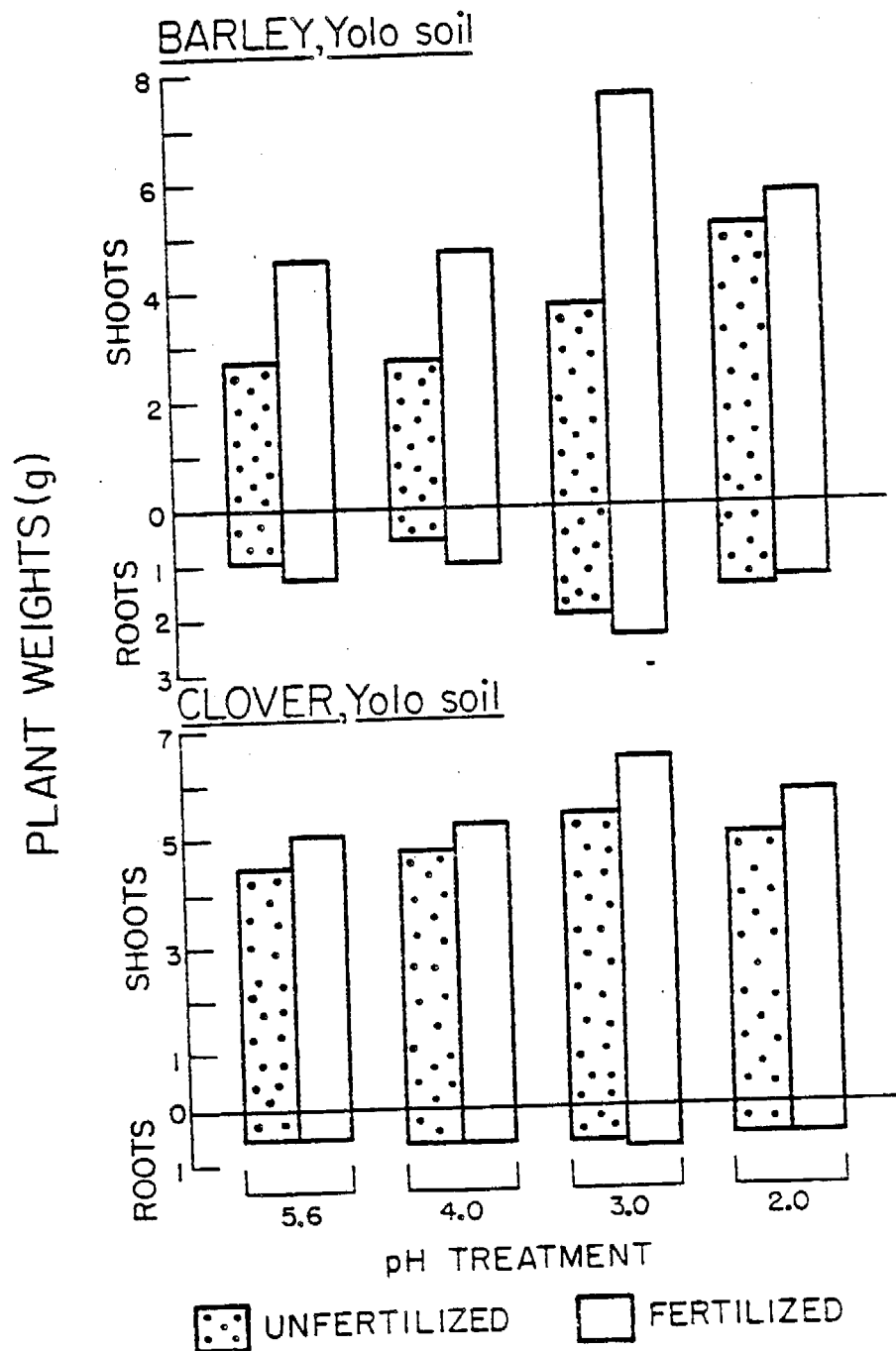
Fig. 8.   Dry-weights of roots and shoots of barley, clover, cabbage and sugar beet growing in Yolo soil, and of soft chess growing in Shaver soil. Effects of both fertilizer and acid treatments are shown. Experiment 2.

-55-
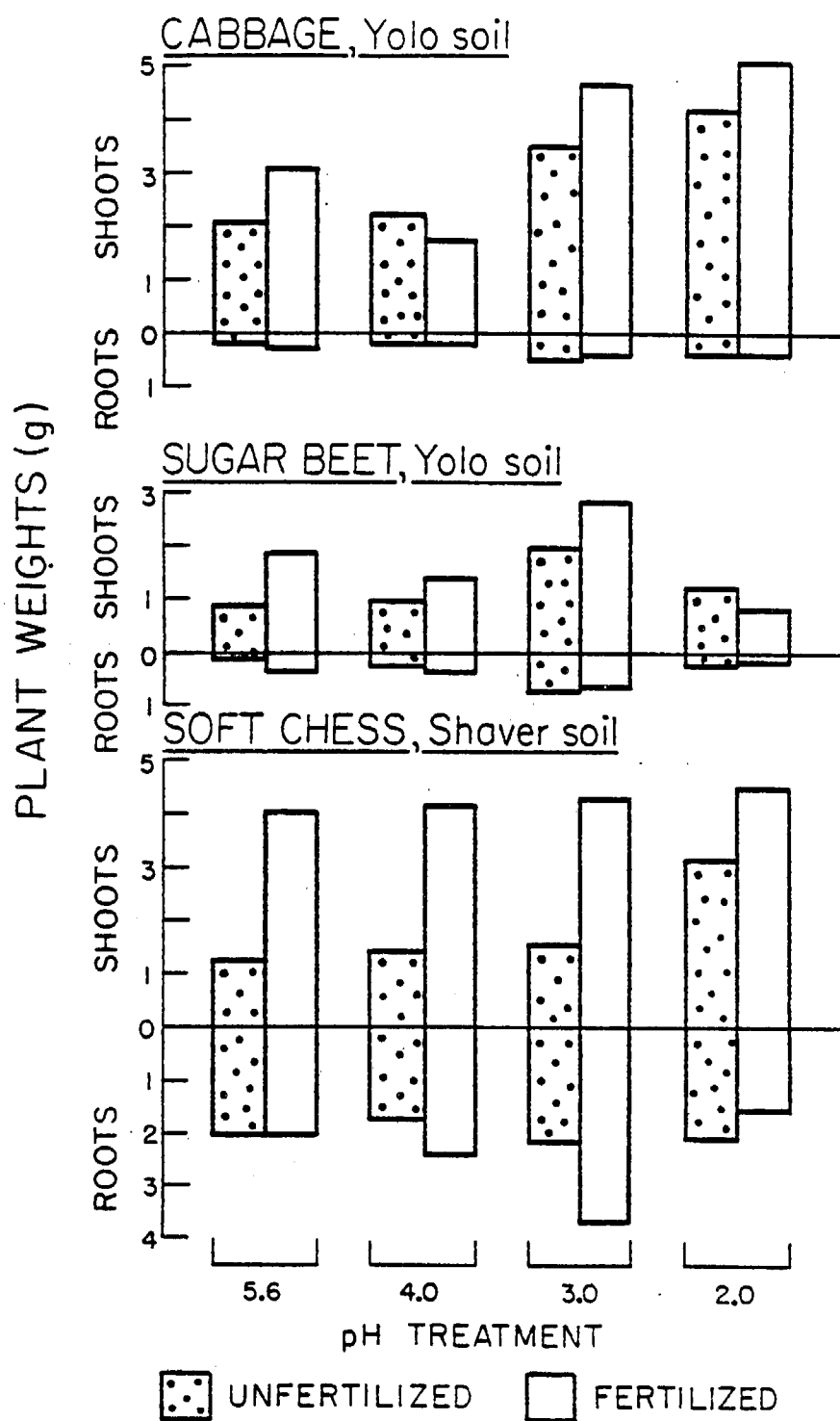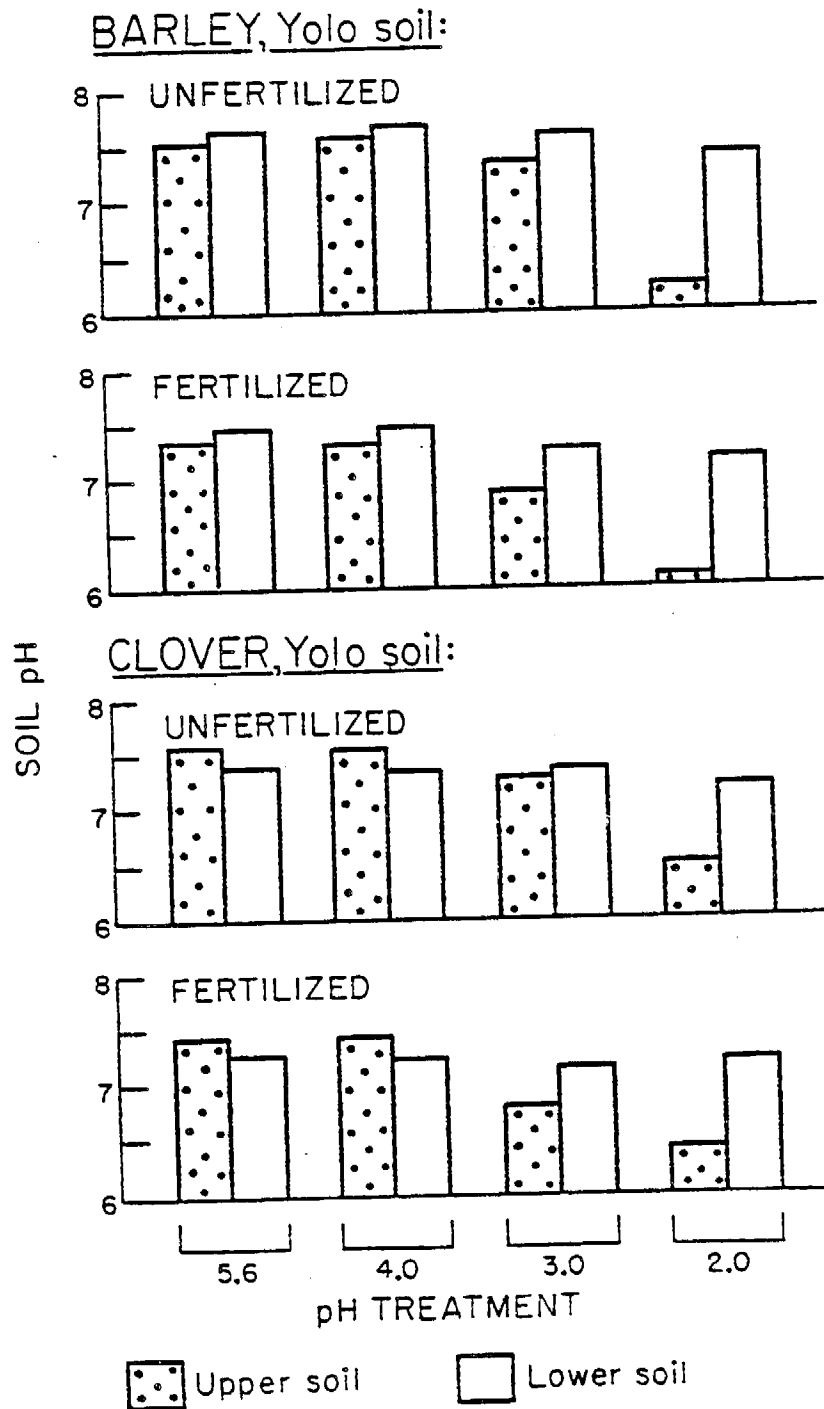
Fig. 8. (continued).

Fig. 9(a)   Soil pH at upper and lower depths; Yolo soil series
throughout, planted with barley, clover, cabbage, sugar
beet, and unplanted control. Effects of both fertilizer
and acid treatments are shown. Experiment 2.
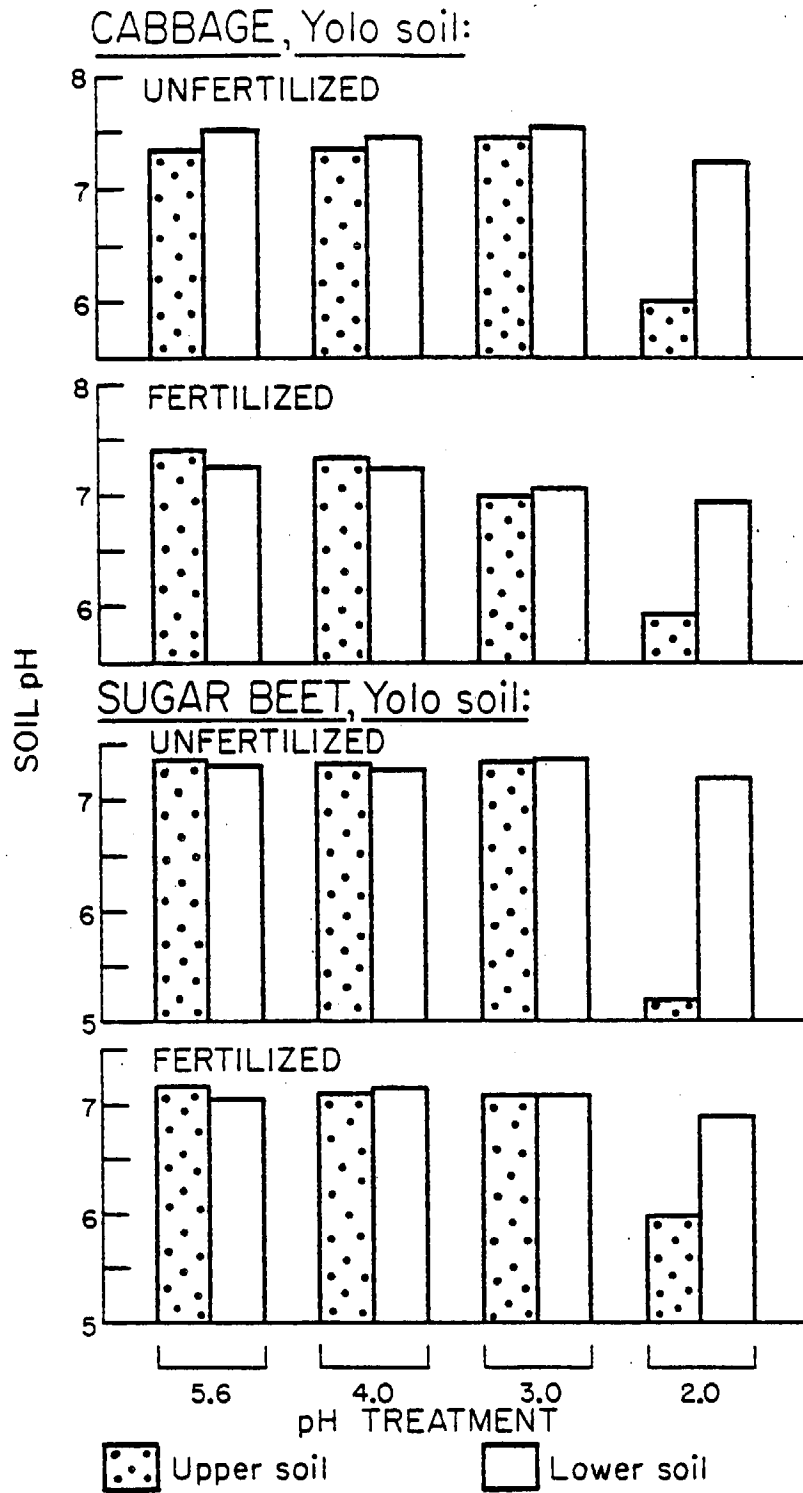
Fig. 9A. (continued)
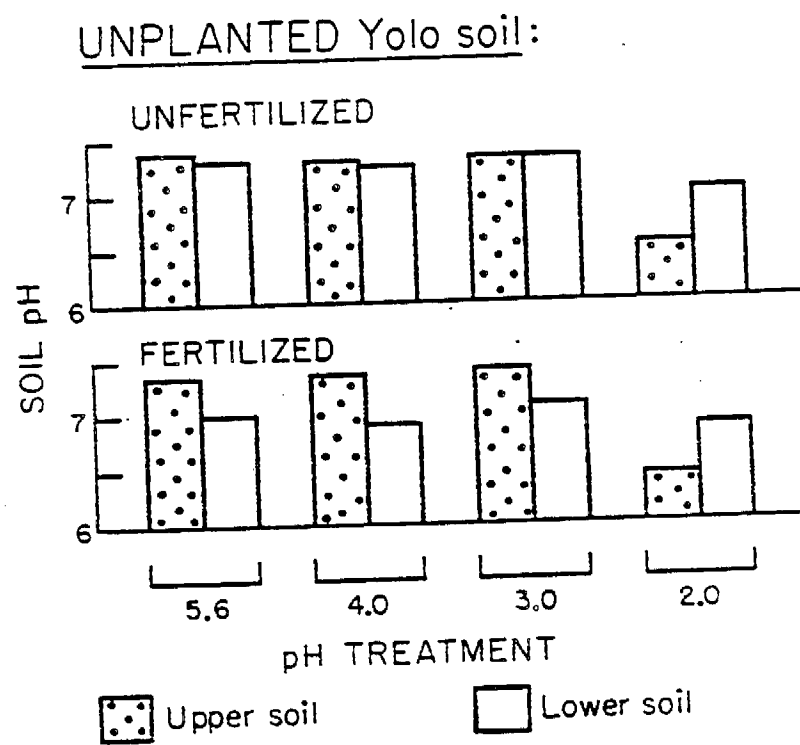
Fig. 9A. (continued).
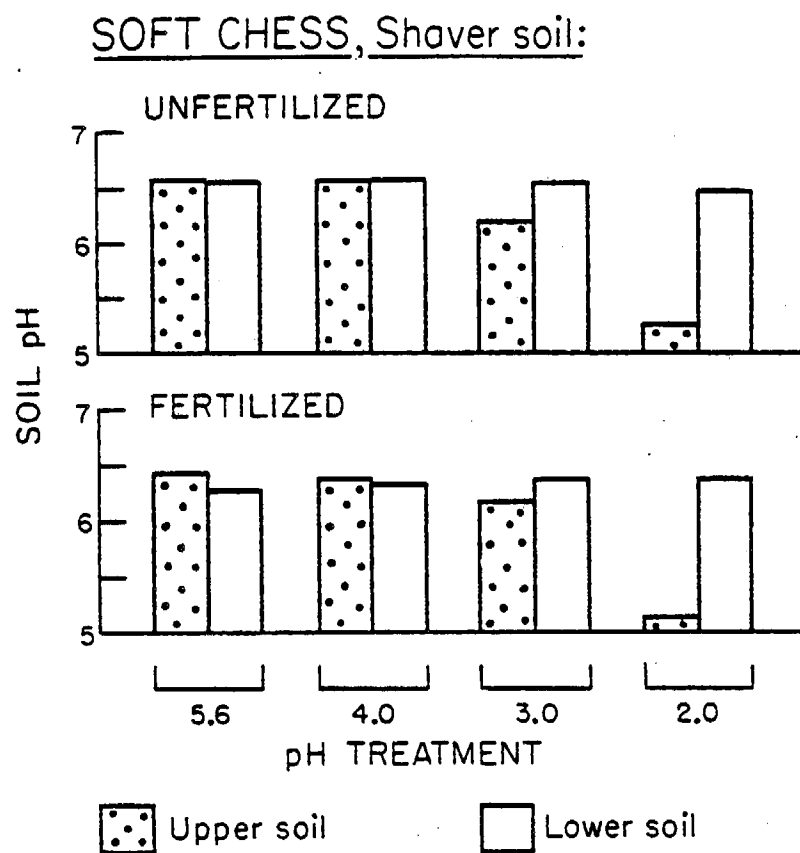
Fig. 9(b) Soil pH at upper and lower depths; Shaver soil series,
planted with soft chess. Effects of both fertilizer and
acid treatments are shown. Experiment 2.

EXPERIMENT 3. Soil leaching to determine relative "sensitivity."

Objective:

To determine the sensitivity to acid rain of important, selected soil of northern California, by ranking them by their relative ionic leaching under controlled conditions.

Methods and Materials:

Soils from a variety of parent materials were selected representing agricultural, range and forest soils, although emphasis was placed on granitic soils from range-land and forest areas, as these soils are likely to be the most sensitive. Samples from the upper mineral horizon were tested. Effects on soils would be greatest in the field where the soil is devoid of vegetation or a protective litter layer, and especially following land-management practices where the surface soil is scarified, e.g. following a commercial clear-cutting in a forest, or conversion of brushland for grazing.

Soil samples were obtained that most closely characterize the soil series selected. Many of the samples tested were actually from those taken of the standard pedon that typifies that particular series; i.e. from the "type location." These samples are stored in the University of California storage facility at Richmond, CA. Other soil samples were taken in the field by us. A particular set of samples were those along an altitudinal transect from the foothills of the Sierra Nevada (Fresno Co.) to the top of the ridge, passing through Shaver Lake; all these soils are developed on granitic material. A summary of the soils tested is given in Table 10.

The soil samples were air-dried, ground and passed through a 2mm sieve before being tested in the Mechanical Vacuum Extractor (Fig. 10). The
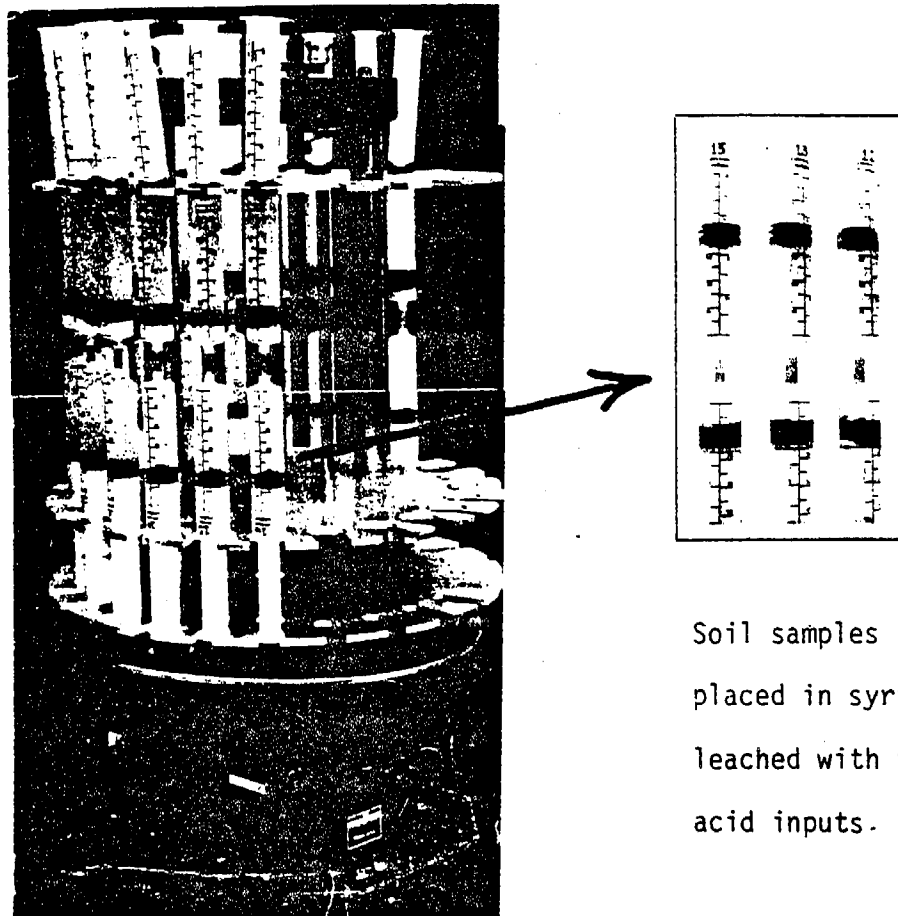
Soil samples
placed in syringes and
leached with various
acid inputs.

Complete unit which can
handle 24 soil samples
simultaneously.

Fig. 10. Mechanical vacuum extractor for studying effects of acid
rain on leaching of soils. Experiment 3.

testing procedure is extremely well-controlled using this device, which is briefly described by Holmgren et al (1977). The device has 24 leaching tubes, thus allowing for adequate statistical replication. There were three replicates per soil series per extract-treatment. The leaching tubes are attached to 60-ml plastic syringes mounted on the periphery of three vertically aligned slotted discs. The plungers are withdrawn at a controlled rate by a variable speed screw-jack that separates the two lower discs holding the plungers and syringe barrels, respectively. Leaching time can be varied from 15 min. to 12 hrs., to simulate the movement of water following either intense rains or steady moderate rains. This mechanically controlled, variable-rate, soil-leaching device, meets the standards required by the USDA's National Soil Survey Laboratory in Lincoln, Nebraska. Chemical data of leachate samples derived from soils tested in this unit allowed good, easily replicated comparisons to be made between soils and between various simulated-acid treatments. A simplified diagram of the acid-leaching procedure is also given in Fig. 2.

For purposes of standardization, the following conditions were used to test the relative leaching of soils under various inputs of simulated acid rain:

Input treatment solutions: a 2:3 mix of H_2SO_4:HNO_3, plus a base-level of other ions (same as described for the plant-spraying experiments). A series of 8 pH treatments were used: 5.5, 4.5, 4.0, 3.5, 3.0, 2.7, 2.3, 2.0. For each 5 g soil-sample placed in the device, 50 ml of treatment acid solution was passed through during a 2-hr period. The resulting leachates were collected and immediately analyzed for pH and electrical conductivity. They were then digested in acid prior to cation analyses. Methods of digestion and chemical analyses are given in Appendix 1.

The total cation exchange capacity (CEC) of each soil was also determined, using the Mechanical Vacuum Extractor with NH_4-acetate; the method is described in Appendix 1. The four main cations (Na^+, K^+, Mg^+, Ca^{2+}) on the CEC were also determined.

Data were punched on computer cards. Summarization of data, and statistical analyses were made using the SPSS package programs, i.e. "Stattistical Programs for the Social Science," (Nie et al., 1975) which are on file at the computer Center, University of California, Berkeley.

The main features of design of this soil-leaching experiment are summarized in Table 11.

Table 10. Soils tested in Experiment 4;
            soil leaching to determine
            relative soil "sensitivity".

Soil Series	Location (county)	Parent material and age
1. Forest Soils		
Aiken	Shasta	basic igneous, moderate
Chawanakee	Fresno	acid igneous, young
Chiquito (1)	Fresno	acid igneous, young
Chiquito (2)	Fresno	acid igneous, young
Cohasset	Shasta	basic igneous, moderate
Corbett	Fresno	acid igneous, moderate
Holland	Fresno	acid igneous, moderate
Josephine	Shasta	sedimentary, moderate
McCarthy	Siskiyou	basic igneous, moderate
Musick	Fresno	acid igneous, old
Neuns	Shasta	basic igneous, moderate
Shaver (1)	Fresno	acid igneous, young
Shaver (2)	Fresno	acid igneous, young
Sheetiron	Shasta	metamorphic, young
Sites	--	metamorphic, old
Sway	Fresno	--
Windy	--	basic igneous, young
2. Range Soils		
Argonaut	Tuolomne	metamorphic, old
Auberry	Fresno	acid igneous, moderate
Dubakella	Shasta	serpentine, moderate
Hesse	Lake	obsidian, moderate
Vista	Fresno	acid igneous, moderate
3. Agricultural Soils		
Corning	Yolo	mixed alluvium, old
Redding	Colusa	mixed alluvium, very old
San Ysidro	Yolo	mixed alluvium, old
Yolo	Yolo	mixed alluvium, young

Table 11. Main features of design of Experiment 4;
soil leaching to determine relative soil
"sensitivity."

Test Soils	A wide variety of soils from agricultural, range and forest areas, derived from various geologic parent materials and age of formation.
Soil Samples	Surface soils (litter layer removed). Many were from soil-series "type-location."
pH Treatments	5.5, 4.5, 4.0, 3.5, 3.0, 2.7, 2.3, 2.0.
Replication	3
Acid Used	2:3 mix of $H_2SO_4:HNO_3$, plus base level of other salts.
Leaching Conditions	5g soil, 50 ml input acid treatment solution, 2-hour.
Soil Chemical Analyses	C.E.C., base-saturation, exchangeable Na, K, Mg, Ca, pH.
Leachate Chemical Analyses	pH, electrical conductivity, Na, K, Mg, Ca, Fe, Mn, Zn, Cu, Al.
Statistical and Mathematical Analyses	Soils ranked according to their relative leaching.

Results and Discussion (Figures 11-17, Table 12).

The author has details of the amount of ions leached from the soils under the various pH-treatments for the ions listed in Table 11. These detailed records are available to the C.A.R.B. on request.

Data of 26 soils were used to create a model which characterizes the response of a soil to acidic inputs. An example of one particular soils' response is shown in Fig. 11A and B; for this Redding soil series, input solutions above pH of about 4 have little effect on the leaching of cations from the soil. Below pH 4, however, the soil can no longer retain its exchangeable cations; H^+ of the output solution rapidly rises also. At pH 2, essentially all the exchangeable cations have been removed, and some mineralization may even be occurring, as the leachate cation concentrations begin to exceed the available cations on the exchange complex (Fig. 11A and B).

In Fig. 11B, the concentration of leached aluminum is given. This element is particularly harmful to aquatic life and can be toxic to plant-roots in a soluble form; its removal from the soil is not so much a problem of "soil depletion" but could be potentially dangerous to plant roots, and to aquatic life once the soil leachate moves in groundwater to streams and lakes.

The model built on the data of the 26 soils tested relates the input H^+ from the acidic input solutions to the output H^+ in the soil leachates and is shown in an idealized form in Fig. 12. The mathematical model was based on log-transformed data of (H^+)-out vs. (H^+)-in; the value k is the mean value ln (k) of points below the inflection point (Fig. 12), and the curvilinear portion of the model was derived separately from the function: log (H^+)-out = a + b log (H^+)-in. The two functions were then combined to form the final
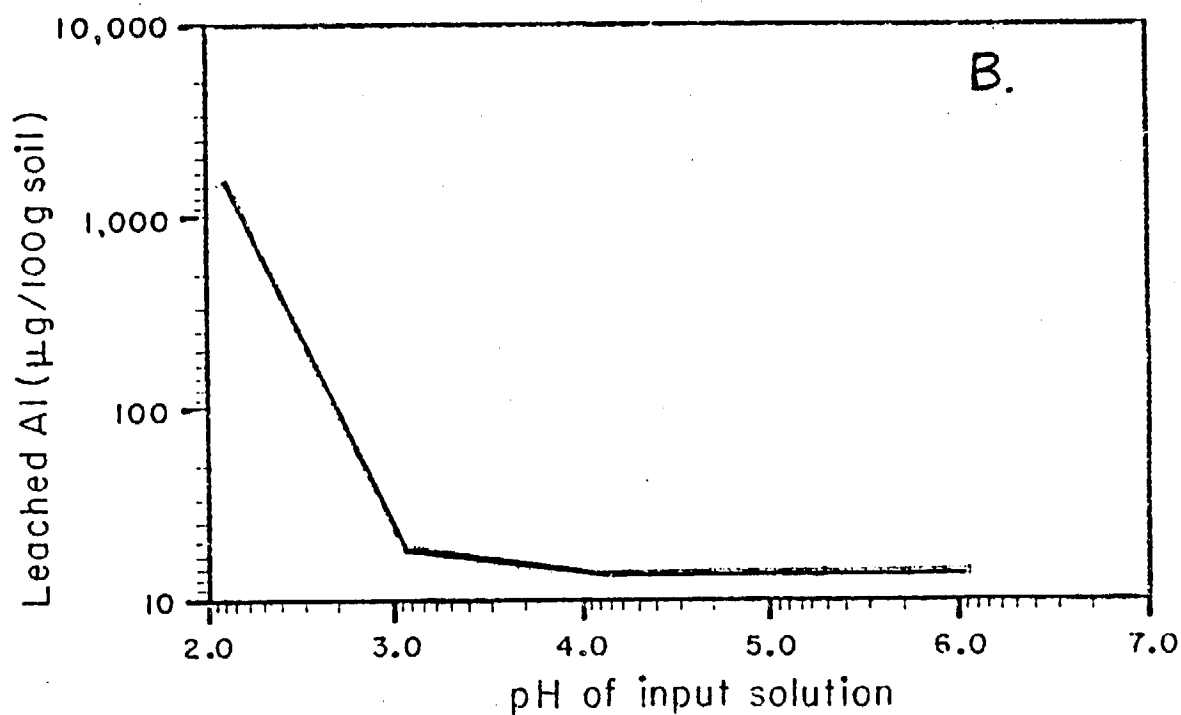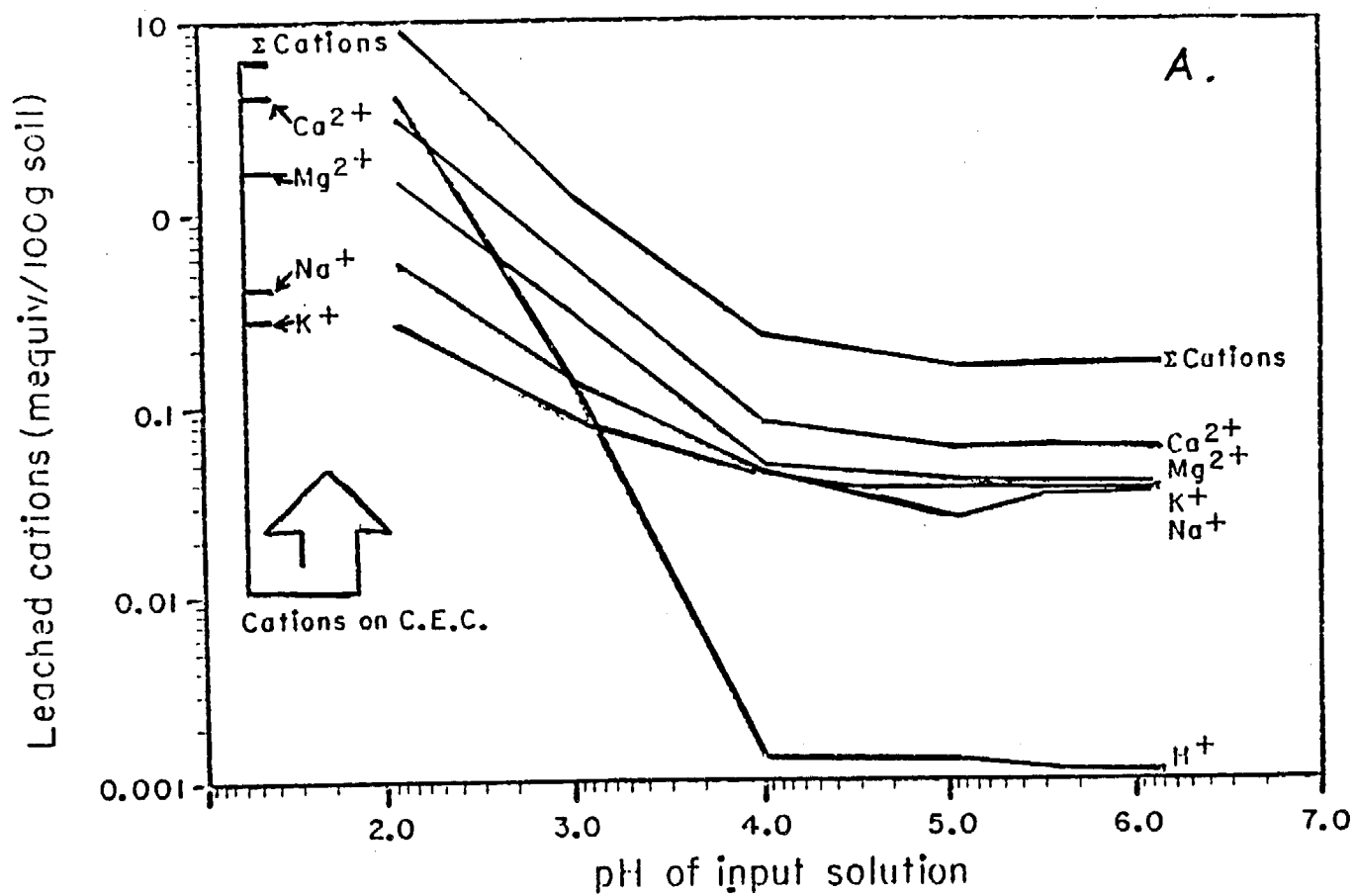
Fig. 11. Example of results of leaching a soil with various aci-
dic inputs. For the Redding soil series, leaching of
the main cations, relative to their amounts on the soil
exchange complex, is shown (A). Leaching of aluminum
is shown on the lower graph (B). Experiment 3.
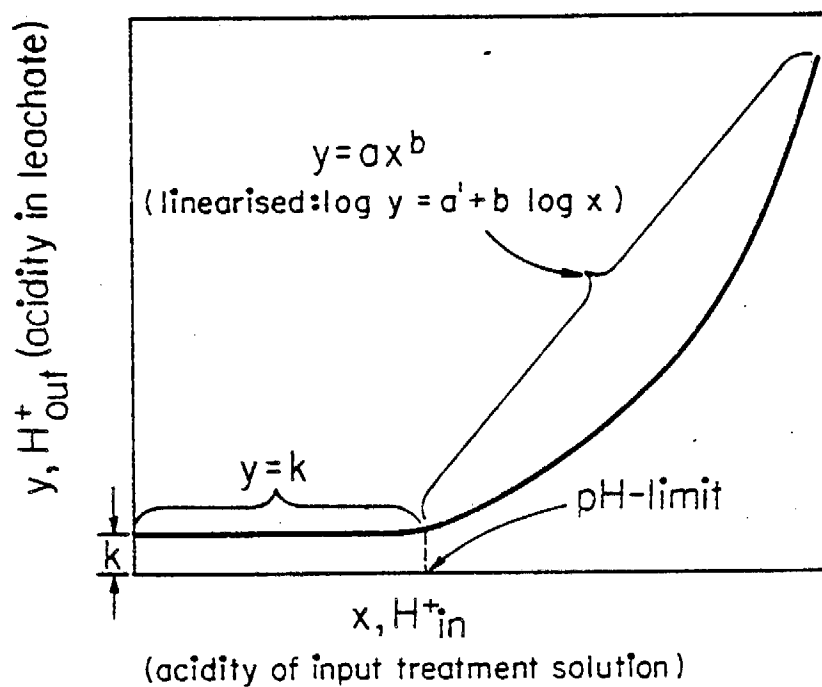
Fig. 12.   Model of input of H+ ions in the acid treatment solutions
versus output of H+ ions in soil leachates.   Experiment 3.

Table 12. Values of k, a', b, and pH-limit, in the model shown in Figure 12, for 26 soils tested. Experiment 3.

Soil series	K	a'	b	pH-limit
		(μeq H^+/l)		
Sheetiron	1.49	7.7×10^{-22}	6.267	2.60
Chiquito (A)	11.93	1.6×10^{-2}	1.419	3.97
Redding	1.22	3.0×10^{-5}	2.121	3.83
Corbett	6.27	1.1×10^{-3}	1.694	3.78
San Ysidro	0.74	3.9×10^{-6}	2.279	3.68
Corning	0.23	7.7×10^{-8}	2.698	3.61
Hess	0.32	4.2×10^{-11}	3.500	3.18
Neuns	3.21	8.2×10^{-11}	3.198	3.00
Chiquito (B)	0.18	1.2×10^{-7}	2.239	3.23
Yola	0.13	1.5×10^{-11}	3.413	3.10
Holland	1.62	1.9×10^{-14}	4.247	2.72
Musick	0.78	3.0×10^{-9}	2.770	2.96
Chawanakee	1.04	1.8×10^{-13}	3.857	2.69
Shaver (A)	1.31	4.5×10^{-7}	2.224	3.09
Sway	1.50	4.7×10^{-6}	1.800	2.94
Shaver (B)	0.51	5.7×10^{-2}	0.293	2.75
Auberry	3.90	1.8×10^{-3}	1.551	2.88
Vista	2.34	2.1×10^{-22}	6.440	2.58
Josephine	1.42	2.5×10^{-12}	3.415	2.56
Sites	2.31	2.1×10^{-9}	2.924	2.91
Windy	2.75	3.8×10^{-2}	0.698	3.33
McCarthy	1.80	2.0×10^{-5}	1.630	2.97
Arken	1.90	5.8×10^{-12}	3.491	2.70
Cohasset	0.76	1.0×10^{-9}	2.713	2.73
Dubakella	2.16	4.5×10^{-25}	6.753	2.34
Argonaut	8.21	6.8×10^{-11}	3.366	2.71

model shown in Fig. 12. In explanation, these terms can be considered separately as follows:

The term "k" is simply a constant describing the quantity of H^+ passing through the soil under conditions of neutralization, or nearly complete consumption of the input H^+. This constant ranges from about 1 to 10 µeq H^+/liter in our experiment.

The term "a" is the intercept on the y-axis when (H^+)-in & (H^+)-out are graphed as logarithms; it is related to "b", which is the slope of the line. The parameter "b" indicates the relationship between H^+-in and H^+-out after the soils cation exchange reservoir is no longer operating i.e., when the cation exchange complex is fully occupied by H^+ ions only. Thus b is a measure of the extent of weathering reactions occurring in the soil over the experimental period. Soils high in easily weatherable minerals would be expected to have low values of b, while those low in such minerals would have high values of b.

The inflection point in the model (Fig. 12) is also of importance, as this indicates the H^+ input at which the cation exchange reservoir is exceeded. It is easily determined by calculating H^+-in when y = k, in the function: log y = a + b log (see Fig. 12). This inflection point is referred to as the "pH-limit" in this report, and was calculated for each of the 26 soils tested.

Values of k, a, b and pH-limit, for the 26 soils tested are given in Table 12.

The next step in the analysis of this data, was to attempt to relate these responses of the soils to acidic inputs to the inherent properties of the soil. Thus values of k, a, b and pH-limit were graphed against such standard soil properties as cation-exchange capacity, soil pH, and base-

saturation, which were also determined for each soil sample. The one relationship showing the greatest correlation was the sum-of-bases versus the pH-limit, and is shown in Fig. 13; this relationship was highly significant $(r = 0.72, OC < 0.001)$. The relationship makes good intuitive sense also. Obviously, once the sum-of-bases on the exchange complex is removed by inputs of H^+, the concentration of H^+ in the output leachate will rise dramatically, i.e. there will no longer be any buffering by the soil to inputs of H^+.

The relationship shown in Fig. 13, provides a useful and simple means to relate "acid sensitivity" of soils to a simple soil property; pH-limit can be considered as good, simple measure of "sensitivity," and the sum-of-bases on the cation exchange complex is a recognized property of soils, which is widely accepted and used and which is easily measured using standard procedures.

Using Fig. 13, then, as a basis of ranking soils according to their sensitivity to acidic inputs, arbitrary boundaries can be used to group soils into low, moderate or high sensitivity classes. Obviously, the placing of boundaries on this continuous function is quite arbitrary and open to discussion and refinement, as data of more soils is included. Nevertheless, it is important to make such generalizations in order to describe landscapes that might be susceptible to ecological damage by acid rain, such as those described by the Canada/U.S. Impact Assessment Working Group in their report (Cowell, Lucas and Rubec, 1981). They used the sum of exchangeable bases as a prime measure to assess both "forest productivity sensitivity" and "aquatic input sensitivity," and the class boundaries they used were: low, >15 meq/ 100g; moderate, 6 to 15 meq/100g; high, <6 meq/100g. When these class boundaries are used on data experimentally derived using our 26 soils (see Fig. 12),
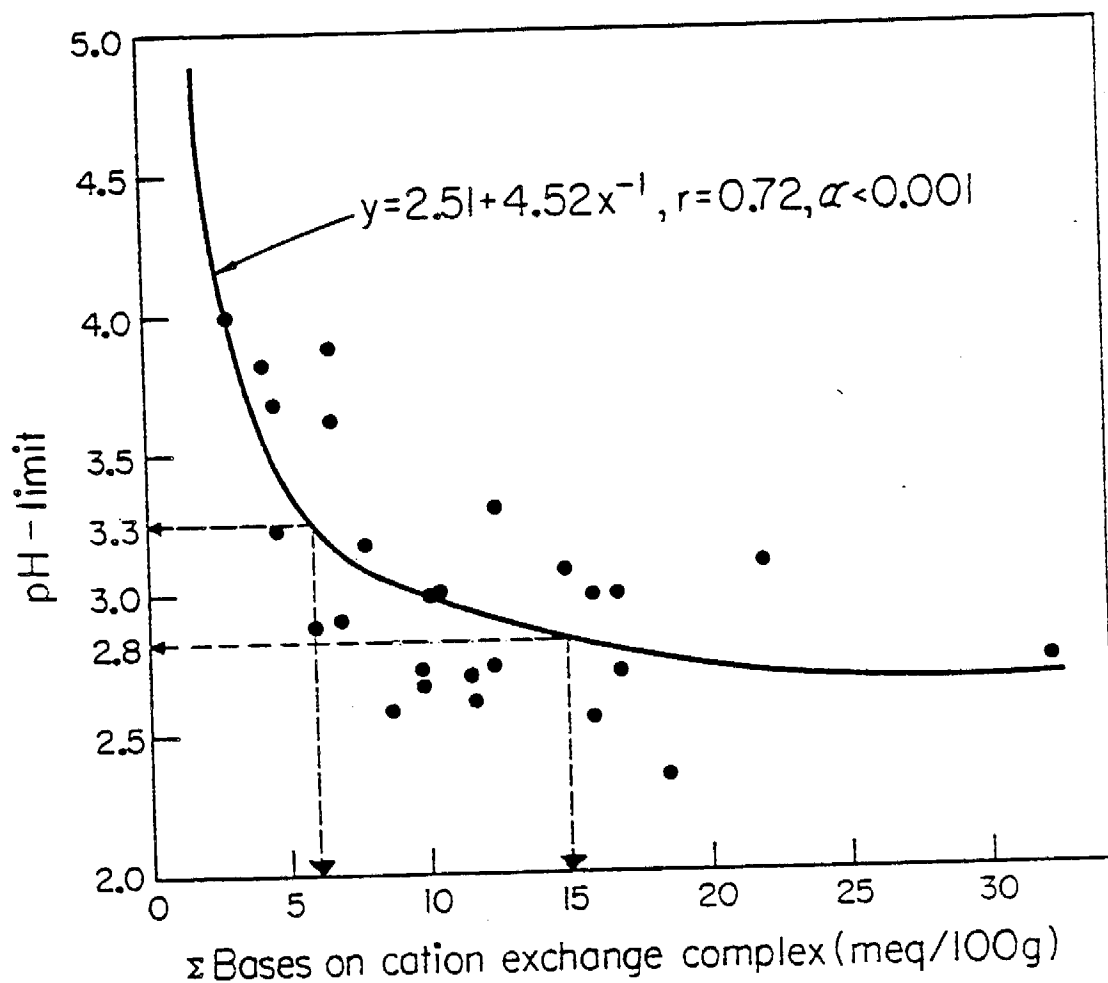
Fig. 13.   Relationship between sum of bases on soil cation exchange complex, and pH-limit which is an index of soil "sensitivity" to acid inputs (see Fig. 12). Arbitrary division of pH-limit classes are also shown (dashed lines). Experiment 3.

(Standard deviations around "pH-limit" for each data point average ±0.05; this error term represents experimental error of the means. Means of 3 replicates for each soil series are shown.)

the corresponding pH-limits are: low, < pH 2.8; moderate, pH 3.3 to 2.8;

high, > 3.3. This implies that highly sensitive soils are those which

are incapable of buffering an acidic input of pH 3.3, whereas soils that

are relatively insensitive to acidic inputs are able to buffer inputs

having pH less that 2.8; soils of intermediate sensitivity are able to

buffer inputs having a pH in the range, 2.8 to 3.3.

Granitic Soils of the Sierran Transect:

Although the total 26 soils can be ranked by thier "pH-limits" and

by their bases on the cation exchange complex (Fig. 13), their relative

placement in the sensitivity series has little relationship to their Soil Series

names. Many more samples would be necessary to adequately characterize

a given Series. However, it might be reasonably expected that related

soil series might exhibit some relationships in regard to sensitivity

i.e. sensitivity might have meaning relative to geographical position or

stage of soil development. With this expectation in mind, the soils of the

"Sierran transect" were analyzed separately. These soils have all been de-

veloped on granitic parent material of the Sierra Nevada, and their pro-

perties are essentially products of the combined effects of precipitation

and temperature, from the edge of the San Joaquin Valley, along an altitudi-

nal transect in a west-to-east direction passing through Shaver Lake to

Kaiser Pass (Fig. 14). This transect has also been studied in some detail

by Jenny, Gessel and Bingham (1949) with reference to rates of decomposition

of soil organic matter, as a function of precipitation and temperature. See

Perry, Zinke and Heater (1964) also.

There is a statistically significant relationship between pH-limit and

elevation for these soils of the Sierran transect (Fig. 15). The most sen-

sitive soils (i.e. those with high pH-limits) are those at high elevation,

where the degree of soil development is minimal and soil depths are shallow
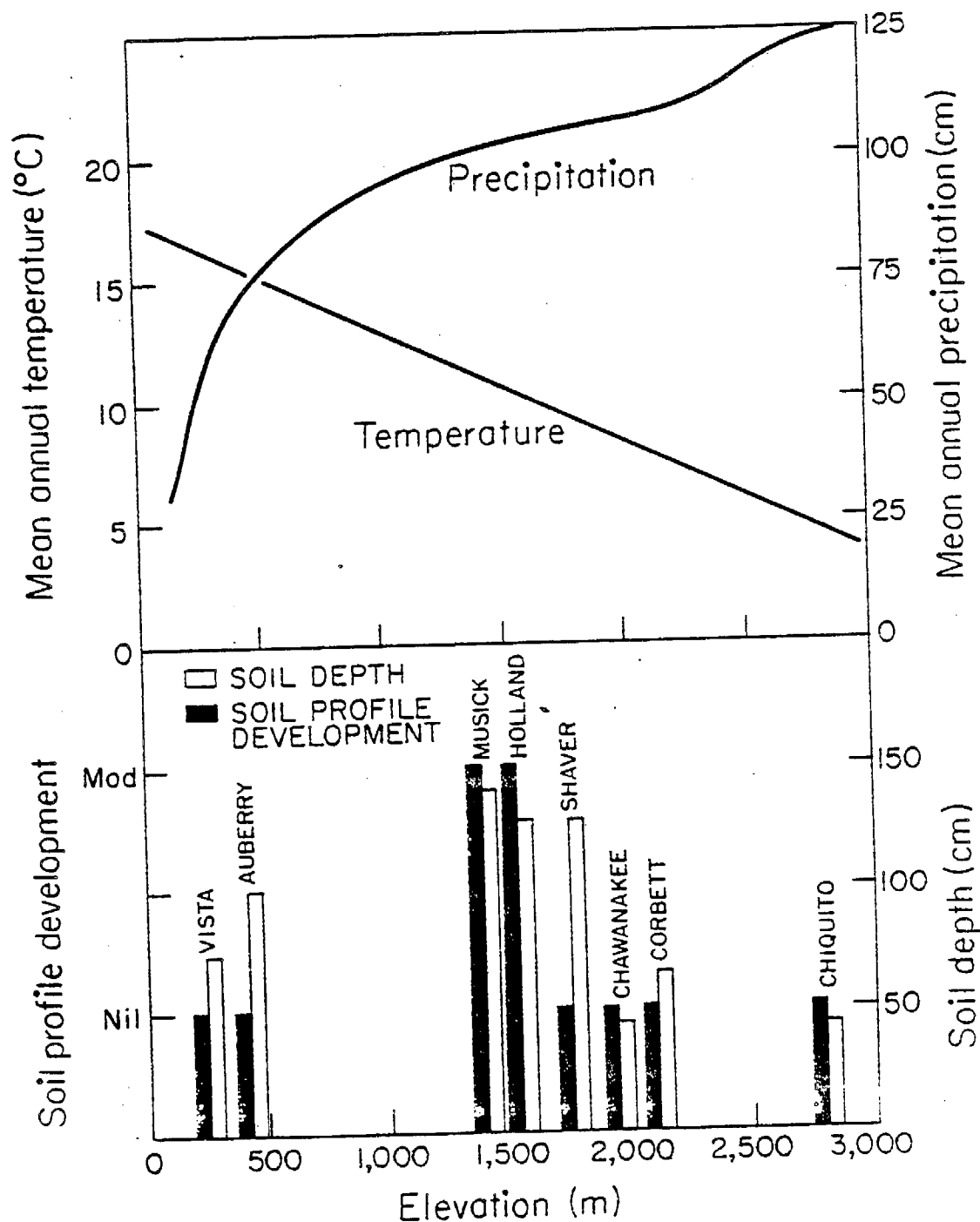
Fig. 14. Climatic and edaphic characteristics across an elevational transect in granitic parent material, from the foothills to Kaiser Pass in the Sierra Nevada. Soil Series in this granitic transect that were tested for "sensitivity" are named in the lower figure. Experiment 3.
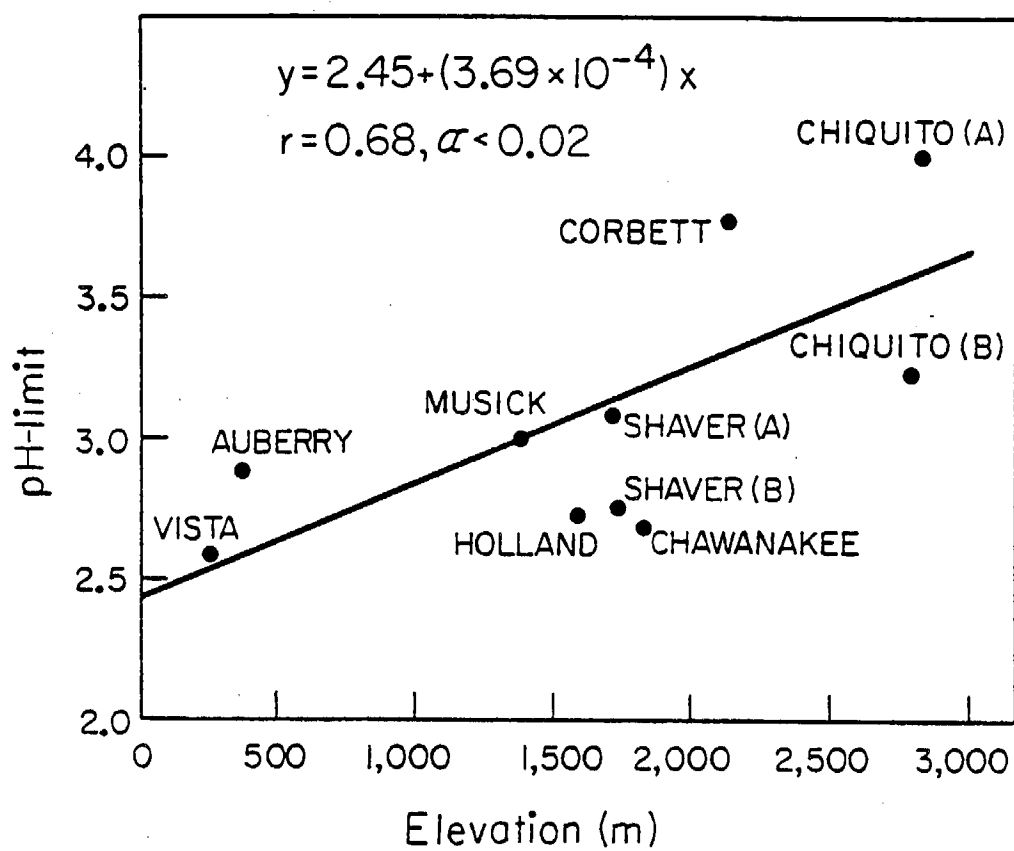
Fig. 15.   Relationship between elevation and pH-limit of soil series
            in the granitic, Sierra Nevada transect. Experiment 3.

and where low temperatures and high precipitation occur (Fig. 14). Soils at low elevations not only have relatively low pH-limits, but also are not subject to as much leaching, due to low precipitation. Soils at mid-elevations have greatest development and depth (Fig. 14), and intermediate sensitivity to acid inputs as shown by pH-limits (Fig. 15).

Similarly, electrical conductivity (a measure of total ion concentration) of leachates from the extreme pH-2 treatment is plotted against elevation in Fig. 16. Once again the relationship shows the sensitivity of the high-elevation soils, that are shallow and have little buffering of the pH-inputs.

In the low pH-leachates, however, H^+ comprises a large proportion of the ions. In terms of characterising the loss of nutrients from soil, a better measure is the sum of the bases (Ca^{2+}, Mg^{2+}, K^+, Na^+) leached from the soil, as shown in Fig. 17. Here a different picture emerges; the relative leaching of bases corresponds to the degree of soil development and soil depth shown in Fig. 14. The most developed soils are those that have greatest amounts of bases leached per 100g soil (Fig. 17); these are the mid-elevation soils. Soil depth and development are less at the low elevations (where precipitation is limiting) and at high elevations (where temperature is limiting), and less amounts of bases are available for leaching from the cation exchange complex.

A second feature is also shown in Fig. 17; the proportions of the total bases on the cation exchange complex that are leached are greatest for the low and high elevation soils, and least for the mid-elevation soils. Thus although leaching of mid-elevation soils by acidic inputs is likely to result in more soluble-nutrients moving in the soil solution and possibly lost in drainage waters, this loss does not represent as great a relative loss of the soil nutrient capital as that of low or high elevation soils.

The results of these granitic soils of the Sierran transect clearly
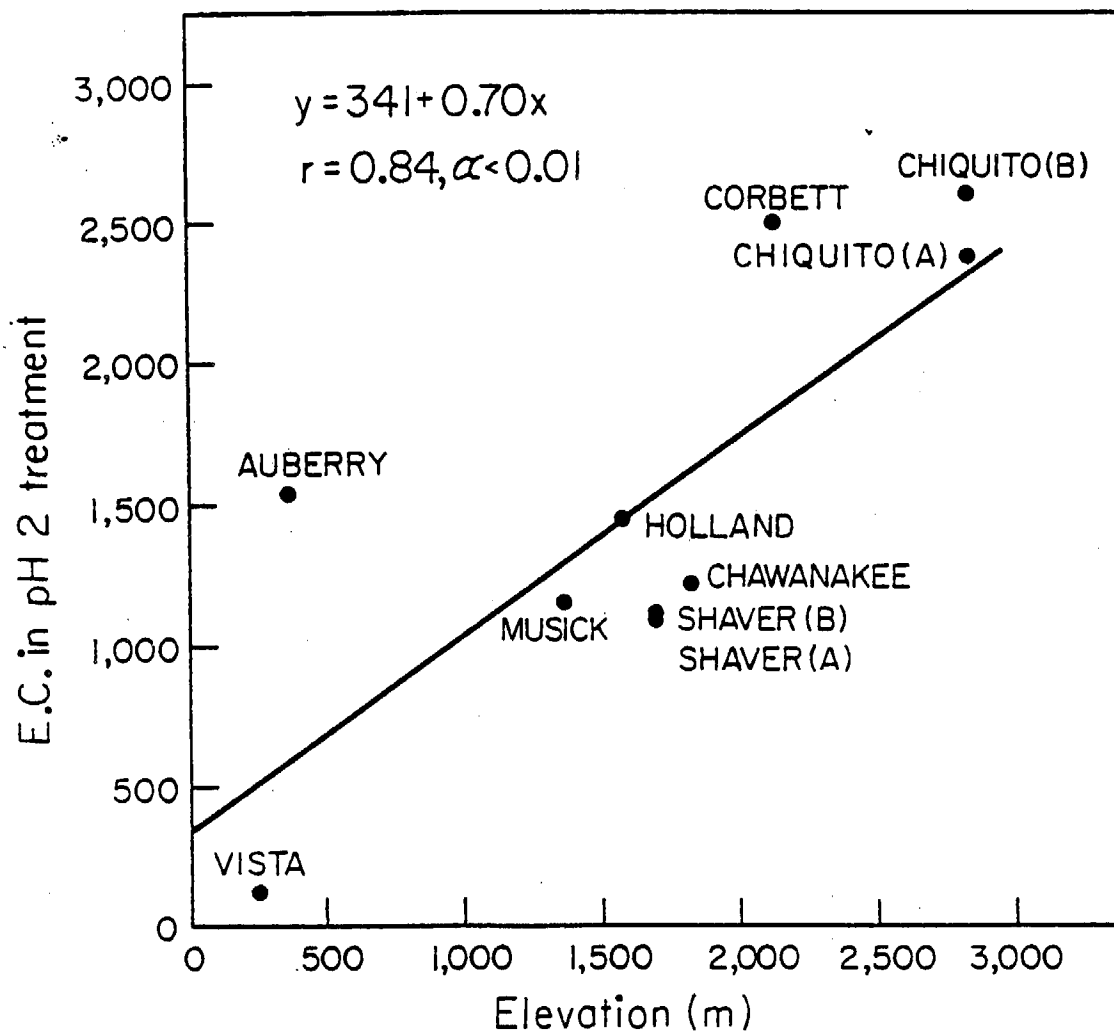
Fig. 16.   Relationship between elevation and electrical conductivity of leachates in the pH 2 treatment, from soil series in the granitic Sierra Nevada transect. Experiment 3.
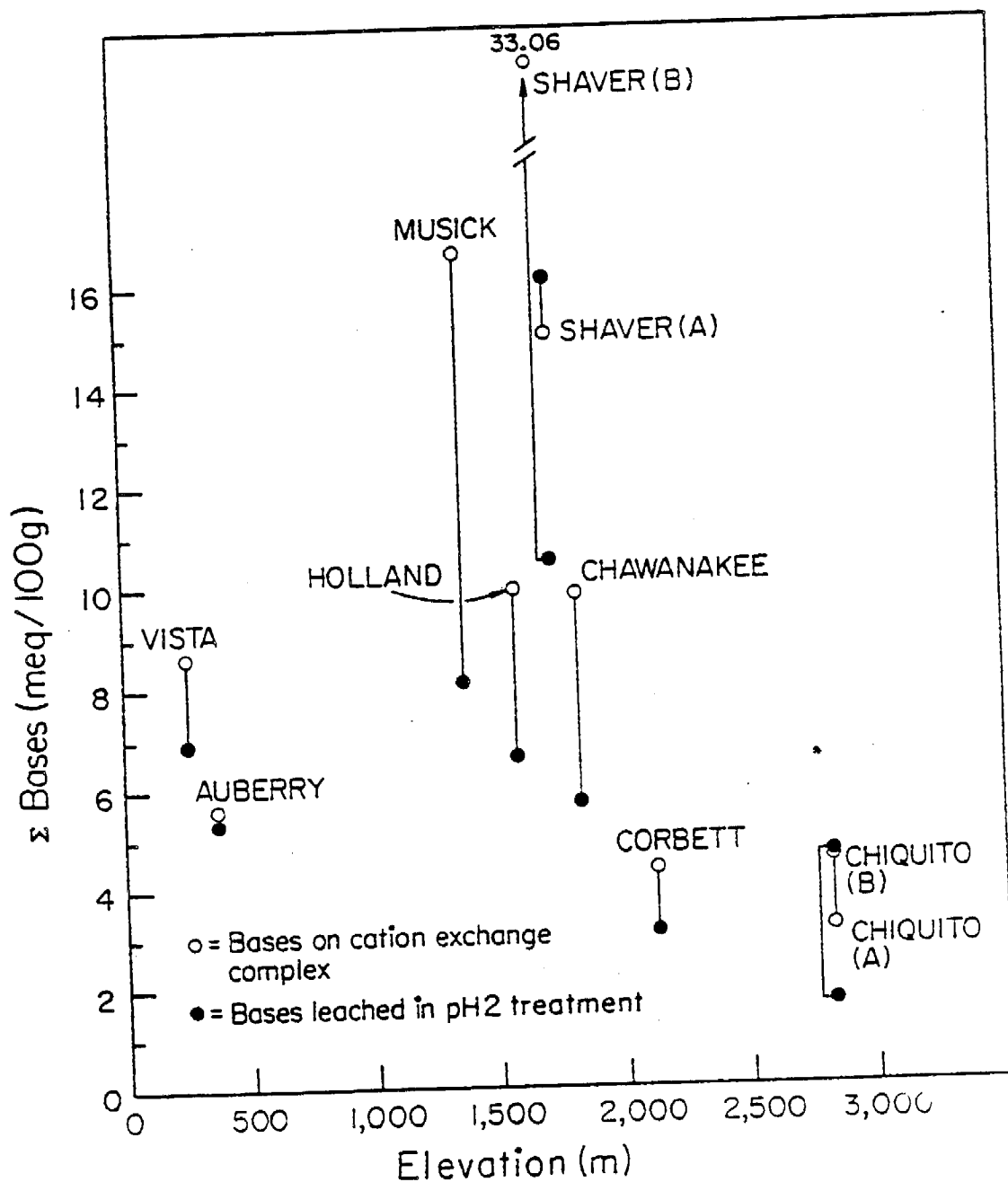
Fig. 17.   Relationship between elevation and the sum of bases (both
on C.E.C., and bases leached in pH 2 treatment) of soil
series in the granitic Sierra Nevada transect. Experiment
3.

show that the degree of soil development, and the relative precipitation

and temperature regimes, determine the relative sensitivity to acidic inputs;

and that "sensitivity" can be described as (a) a measure of the depletion of

the soil nutrient capital, and (b) a measure of the amount of nutrients leach-

ed in the drainage waters. These two measures of sensitivity are not necessa-

rily the same, and must be distinguished when a soil series or given geograph-

ical area is categorised.

The soils of the Sierran transect that are most sensitive are those of

high elevation. Such soils typically are shallow with minimal soil depth

and degree of development, and are subject to high amounts of precipitation.

Geographically, they are located in areas near the tree-line which are

used as water-catchments and which contain many oligotrophic lakes. Thus,

leaching of bases and other elements such as Al from such areas not only

poses a serious threat to depletion of soil nutrient reserves, but also poses

a threat to water quality and aquatic life. The high elevation areas, there-

fore qualify as sensitive to acidic inputs by either definition of "sensiti-

vity." The mid-to-high elevation areas are those of prime forests which,

in contrast to agricultural areas, are not intensively managed, and not as

amenable to practices designed to mitigate effects of acidic inputs (e.g.

such as addition of lime); once damaged, effects are likely to be long-lasting.

Other soils:

Some soils in agricultural areas (such as San Ysidro, Redding, Corning)

have high pH-limits (Table 12) and therefore are relatively sensitive to aci-

dic inputs. However, they are less likely to be seriously affected, as irri-

gation and fertilization practices would far outweigh the influence of acidic

atmospheric precipitation. The leaching of bases and other ions such as Al^{3+},

however, would be accelerated by acidic inputs, and would thus increase the ionic concentration of drainage waters.

EXPERIMENT 4 Effects on forest tree species.

Objective: To determine the effect of acid rain on seed germination and on growth of coniferous forest tree species growing in native soil. This experiment has two components:

(a) effects on seed germination and very early seedling growth;

(b) effects on two-year-old seedlings at the "outplanting" stage.

Materials and Methods:

(a) Seed was obtained from the U.S.D.A. Forest Service, Forest Tree Genetics Station at Placerville, CA. Seed of Douglas fir (Pseudotsuga menzesii) and sugar pine (Pinus lambertiana) from various locations were obtained. The two primary locations were from the southern end of the Cascade Mts. and from the mid Sierra Nevada. Seed was also identified by individual tree or stand, and usually by elevation also, at each main location (Table 13). Thus, the experimental design was established so that possible within-species sensitivity to acid rain might also be examined i.e. seed from each individual source was treated with each pH input.

Seed was given 60 days of a cold-moist pre-treatment ("stratification") to enhance uniform germination, as follows: seed was soaked overnight in Captan fungicide solution (1 teaspoon per liter). Moistened seed was then placed in perforated plastic bags in a refrigerator at about 3°C for 60 days (USDA Forest Service, 1974).

Seed was then germinated in sterile greenhouse sand in plastic trays, moistened and kept moist by acid treatment solutions of pH 5.6, 4.0, 3.0 and 2.0. These acid-treatment solutions (with a base level of other salts) were identical to those used in the other plant-spraying experiments. Details of the experiment follow: Following "stratification," seeds were rinsed with

distilled water, then sown by hand in the plastic trays (26 x 52 x 7 cm in dimension), with radicle end-down, spaced about 2.5 cm apart (i.e. about 120 seeds/ft^2). Seeds were sown in sterile sand, pre-moistened with the appropriate acid treatment solution. Seeds were covered with about 4-5 mm of sand. Cheesecloth was placed on top of the sand until germination, to prevent the acid-spraying from disturbing the germinating seeds. Each seed lot was randomly separated into four groups and sown in separate trays. The trays were placed in a lath-house for the duration of this germination test.

Percentage germination was determined for each seed-lot by daily counting Full details of methods of raising tree seed are given in the "seed manual" (USDA Forest Service, 1974). On the 17th day since planting, fungicide was sprayed on the trays to prevent "damping off" fungi (Dexon 100, 1.63g/ 3 gal., and Benlate 100, 2.26g/3 gal.).

The main features of design of this germination experiment are summarised in Table 14.

(b) The plants in pots were treated using the same equipment as described in Experiment 2; the spray treatments, and the Shaver soil series was also the same, although two separate soil lots were used which were collected on separate occasions from different areas.

Two test-species were used, which are both extremely important, common commercial tree-species; Douglas-fir (Pseudotsuga menzessii), from seed source near Corvallis, Oregon, and ponderosa pine (Pinus ponderosa), from both Siskiyou Co., and east of Fresno, California. Seedlings of these two species were purchased from H-H Forest Tree Nursery, Sebastapol, California, and were 2-year-old nursery stock at the "outplanting stage." Thus, we used typical commercial stock that was raised in a typical tree nursery. It was bare-rooted stock that had been kept refrigerated since "lifting" from the nursery bed. The main features of the experiment are summarized in Table 15.

Table 13. Details of sources of Douglas-fir and sugar pine seed used in germination tests. Experiment 4(a).

FROM: UNITED ATES DEPARTMENT OF AGRICULTURE
Forest Service
PACIFIC SOUTHWEST FOREST & RANGE EXPERIMENT STATION
Institute of Forest Genetics
2480 Carson Road, Placerville, California 95667

TO: Dr. J. G. McColl
UCB
Berkeley, CA

Page 1 of 2 pages
By Fryer Date 2/6/81

Seed _X_ Pollen___ Scions___ Seedlings___

REFERENCE: Seed pulled at request of Dr. John Fryer who delivered seed

Species or Hybrid	Lot or Plot	ORIGIN				Crop year	Quantity	More information attached
		Locality	Latitude	Longitude	Elev 'ft.'/Meters			
Pinus								
lambertiana	L-Eld-41-12	Big "X" Mountain, Slab Cr. Cable Point Rd, ElDorado, CA	49°00'	120°38'	3400'	1980	100	T11N, R12E, S?
"	L-Eld-41-14	"	"	"	"	"	"	"
"	L-Eld-41-15	"	"	"	"	"	"	"
"	L-Eld-41-17	"	"	"	"	"	"	T8N, R13E, S2
"	L-Eld-40-1	Big Mtn., Omo Ranch, ElDorado Co., CA	38°34'	120°31'15"	4000'	9/16/8?	"	
"	L-Eld-40-4	"	"	"	"	"	"	
"	L-Eld-40-7	"	"	"	"	"	"	
"	L-Eld-40-9	"	"	"	"	"	"	
"	L-Eld-40-10	"	"	"	"	"	"	
"	L-Eld-40-11	"	"	"	"	"	"	
"	110-K177 (?)	Siskiyou Co, CA	41°05'	123°06'	3600-428	"	50	
"	110-K194	"	"	"	"	"	"	
"	110-K197	"	"	"	"	"	"	
"	110-K198	"	"	"	"	"	"	
"	110-K199	"	"	"	"	"	"	
Pseudotsuga								
menziesii	Lot KA	Sly Park, ElDorado Co, CA	38°40'	120°33'	3370'	8/29/7?	500	T11N, R.E.S15
"	" KB	Fresh Pond, ElDorado Co, CA	38°45'30"	120°32'30"	4100'	8/30/7?	400	
"	" CJ	Klamath NF, Oregon	—	—	1500'		100	T17N, R.E.S15
"	" FU	"	—	—	2100'		100	
"	" DA	"	—	—	3200'		100	

PLANT MATERIAL TRANSMITTAL

FSW AIDOOS-5 (Rev 12/60...)

Table 13. (continued).

Details of sources of Douglas-fir and sugar pine seed used in germination tests. Experiment 4(a).

Page 2 of 2 pages
By Fryer Date 2/6/81

FROM: UNITED ATES DEPARTMENT OF AGRICULTURE
Forest Service
PACIFIC SOUTHWEST FOREST & RANGE EXPERIMENT STATION
Institute of Forest Genetics
2480 Carson Road, Placerville, California 95667

Seed X Pollen ___ Scions ___ Seedlings ___

TO: Dr. J. G. McColl
UCB
Berkeley, CA

REFERENCE: Seed pulled at request of Dr. John Fryer who delivered seed

| Species or Hybrid | Lot or Plot | ORIGIN | | | | | Crop year | Quantity | Additional Information Attached |
		Locality	Latitude	Longitude	Elev. -ft. Meters			
Pseudotsuga									
menziesii	Lot CR	Klamath NF, Oregon	--	--	3600'		100	
"	" CZ	"	--	--	3200'		100	
"	" CU	"	--	--	3300'		100	
"	" EZ	"	--	--	3700'		100	
"	" JP	"	--	--	4000'		100	
"	" LA	"	--	--	3200'		100	
"	" EU	"	--	--	2000'		100	
"	" HI	Pilot Creek Eldorado, CA	38°60'	120°30'	4550'	2/2/60	100	

Table 14.   Main features of design of experiment 4(a);
effects on germination of Douglas-fir and
sugar pine.

Test species	Douglas (Pseudotsuga menzesii) and sugar pine (Pinus lambertiana).
Germination media	Sterile sand, treated with acid-treatment solutions.
pH treatment	5.6, 4.0, 3.0, 2.0
Acid used	2:3 mix of H_2SO_4: HNO_3, plus base-level of other salts.
Data obtained	Germination percentage, by daily counts of germinated seeds. Within-species differences, by geographical location, also studied.

Table 15. Main features of design of Experiment 4(b); effects on Douglas-fir and ponderosa pine seedlings.

Test species	Douglas-fir (Pseudotsuga menzesii) and ponderosa pine (Pinus ponderosa); 2-year-old nursery stock at "out-planting" stage.
Test soil	Shaver soil series, from two locations in the field. Unfertilized.
pH treatments	5.6, 4.0, 3.0, 2.0
Replication	12
Acid used	2:3 mix of H_2SO_4: HNO_3, plus base-level of other salts.
Treatment period	12 weeks
Plant data	Growth increment i.e. growth of apical meristem and dry weight of new needles.
Soil data	Surface-soil sampled for pH changes.

Results and Discussion (Table 16, 17, 18 and Figures 18 and 19)

(a) Effects on seed germination and very early seedling growth.

Although the applied treatment solutions had pH values of 5.6, 4.0, 3.0 and 2.0, the sand in which the seed germinated buffered the pH of the treatment solution, resulting in the pH regimes of the germination media as shown in Table 16. Thus, the pH environments of the germinating seeds varied between those of the pH of the input solutions and those of the sand-solution media. The pH environments of the resulting seedlings, however, were those of the input solutions, as the treatments were applied by spraying from above.

Douglas-fir:

None of the Douglas-fir seed from the Klamath National Forest, Oregon, germinated (see Table 13 for details of seed sources); this is not attributed to any of the applied treatments, but merely due to poor seed. Thus, no comparisons could be made between the two main seed sources (Klamath N.F., Ore., and El Dorado, California). There were also no detectable differences in germination between seed lots at El Dorado; thus, all seed of Douglas-fir was treated as one group and results presented as a whole in Fig. 18. Most germination occurred between the 10th and 20th day from planting. There was no difference in germination between the pH 5.6, 4.0 and 3.0 treatments, but pH 2.0 did have a significant effect. Germination dropped from about 90% to 60% in the pH 2.0 treatment (Fig. 18). In addition to this effect, the pH 2.0 treatment also killed some of the small seedlings that germinated, as indicated by the dashed (--) line of "% remaining" in Fig. 18. These deaths apparently were caused by fungal attack, and a preliminary examination of dead seedlings revealed that the causal fungi were not the usual "damping-off" fungi. Apparently, the cuticles of the stems of the small seedlings were damaged by the low-pH treatment, allowing subsequent fungal attack to occur.

Seedling deaths in the other treatments were negligible (Fig. 18).

<u>Sugar Pine</u>:

Different results were obtained for germination of sugar pine (Fig. 19). Germination occurred more slowly, probably because it took longer for imbibition of water to occur through the thicker seed coats of Sugar pine (compared to Douglas-fir, Fig. 18). Germination per cent did not differ between pH treatments. However, there were significant deaths of small seedlings in the pH 2.0 treatment, and in this regard, the results were similar to those of Douglas-fir (compare Figs. 18 and 19). There were not detectable differences in germination, or seedling deaths, between seed lots of Sugar pine (listed in Table 13).

Table 16. Acidity of the germination media in Experiment 4a.

	pH (mean ± S.D.)			
Treatment solution	2.0	3.0	4.0	5.6
Sand-solution media:				
Wet[1]	2.58 ± 0.07	4.68 ± 0.15	7.48 ± 0.12	7.52 ± 0.17
Dry[2]	2.69 ± 0.14	4.71 ± 0.11	7.59 ± 0.29	7.77 ± 0.22

[1]pH taken two hours after spraying treatment.

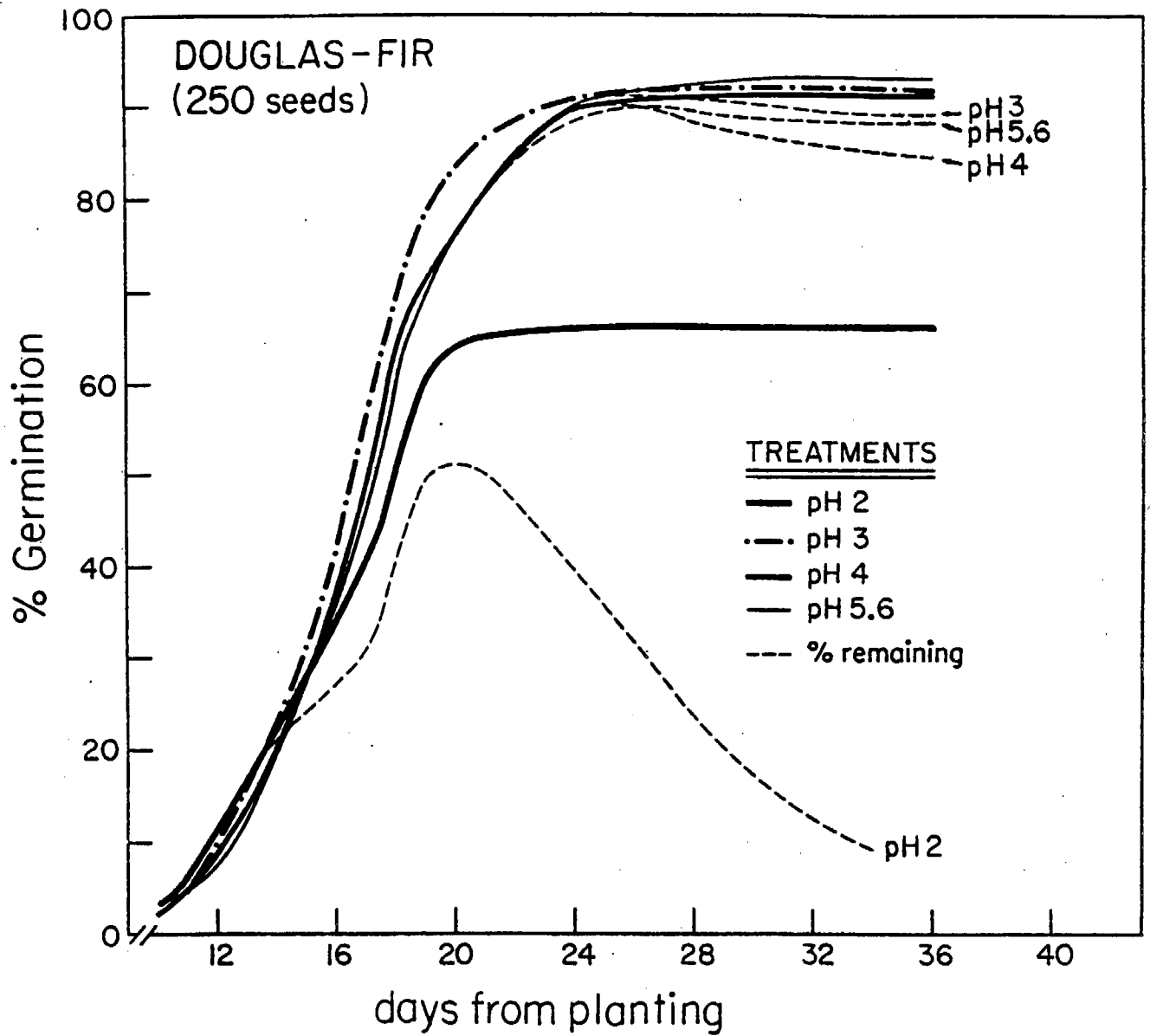[2]pH taken two days after spraying treatment.

Fig. 18. Germination of Douglas-fir seed, and response of subsequent very small seedlings, treated with solutions of different acidity. Experiment 4(a).
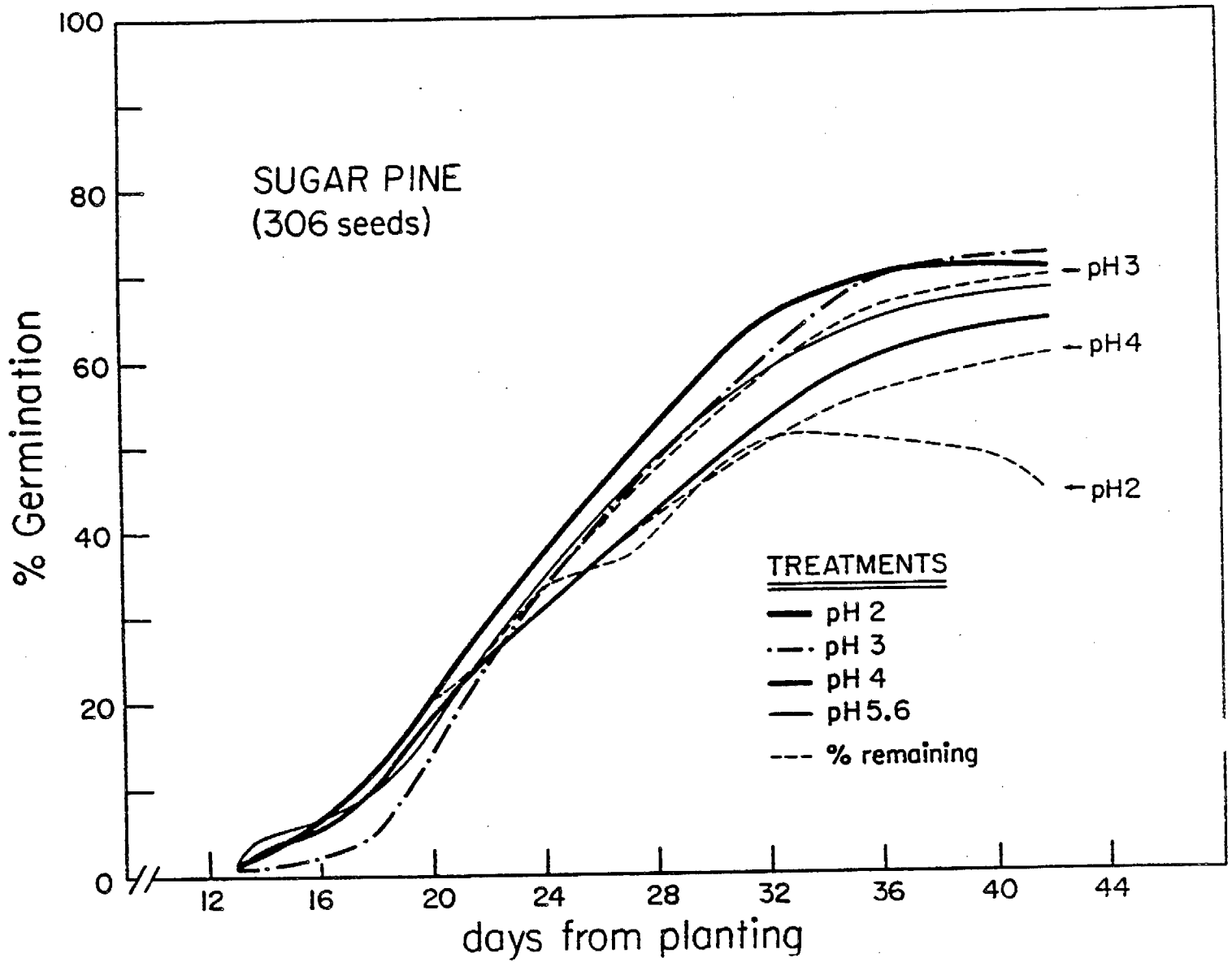
Fig. 19. Germination of Sugar Pine seed, and response of subsequent very small seedlings, treated with solutions of different acidity. Experiment 4(a).

(b) Effects on two-year-old seedlings at the "outplanting" stage.

Bare-rooted seedlings were planted in the test soil (Shaver) on 4-16-81 and acid-spray treatments began on 5-5-81. During the flush of spring bud-break and subsequent needle-elongation, measurement of growth was made on 6-22-81 and 7-23-81 (Table 17). For Douglas-fir, the total length of the apical growth was measured. For Ponderosa pine, the lengths of three of the largest developing needles were measured. Although means slightly varied between pH-treatments and between soil lots, the standard deviations around the means were large, and statistically significant differences between means were not apparent (Table 17).

As a better measure of the growth of new shoots, dry-weight of new needles were determined at the termination of this experiment on 7-30-81. These dry weights (Table 18) confirmed the needle-length measurements (Table 17), in that variations around mean values were large and that there were no clear effects between pH-treatments.

These conifer species have "overwintering buds", i.e. meristematic buds that are formed the previous season, enclosed in a protective sheath. Thus, the acid treatments during the spring flushing period would not affect the formation of these buds, but would only affect cell-elongation of the meristematic cells, not cell number. Results obtained in this experiment indicate that cell elongation was unaffected also. However, in the pH 2.0 treatment, both Douglas-fir and Ponderosa pine became limp, showing signs similar to that of wilting, and needles (both old and new) were spotted, browned at the tips, and many abscissed. It was obvious, therefore, that the most severe treatment (pH 2.0) had gross deleterious effects on the seedlings, even though shoot length and weight were unaffected.

Soil samples were also taken at the termination of the experiment on 7-30-81; surface samples were taken from three replications of each species-

treatment combination. Results are as follows:

Treatment pH	2.0	3.0	4.0	5.6
Soil pH	3.57 ± 0.10	5.93 ± 0.20	5.99 ± 0.15	6.54 ± 0.13

$\binom{\text{Mean} \pm \text{standard}}{\text{deviation}}$

Soil pH was decreased in all treatments, compared to the "control" of pH 5.6, a result not unexpected, and well-documented for the earlier Experiments 1 and 2 in this report. Only in the pH 2.0 treatment did the pH drop markedly to 3.57.

This experiment with conifer tree seedlings showed that direct effects of acid spraying were minimal, if not undetectable, within the range of acid rain experienced under field conditions. However, it tells little about effects of mild acidity on the developing overwintering bud, or about the cumulative effects of decreasing soil acidity on soil fertility and subsequent tree productivity. Such effects, even though of small magnitude over one growth-season, may have serious consequences over many years. Thus, it is recommended that long-term studies must be conducted that address these questions.

Table 17. Length of new needles of Douglas-fir* and ponderosa pine under different acid treatments. Experiment 4(b) (Mean lengths in m. m. ± standard deviations; n=12).

(a) Measurements taken 6-22-81.

Species and seed source	Soil (both Shaver)	Treatment pH			
		2.0	3.0	4.0	5.6.
Douglas-fir, 252	A	66 ± 21	57 ± 23	72 ± 29	51 ± 28
	B	57 ± 27	65 ± 27	76 ± 22	84 ± 30
Ponderosa pine, 310	A	53 ± 7	52 ± 11	59 ± 19	55 ± 9
	B	49 ± 14	61 ± 19	64 ± 16	61 ± 13
Ponderosa pine, 531	A	58 ± 10	60 ± 18	60 ± 9	52 ± 10
	B	71 ± 12	63 ± 9	70 ± 21	62 ± 14

(b) Measurements taken 7-23-81.

Douglas-fir, 252	A	72 ± 21	57 ± 25	76 ± 29	57 ± 26
	B	66 ± 23	69 ± 29	82 ± 24	78 ± 27
Ponderosa pine, 310	A	100 ± 19	88 ± 26	91 ± 90	82 ± 16
	B	107 ± 15	98 ± 18	102 ± 24	88 ± 17
Ponderosa pine, 531	A	85 ± 17	83 ± 16	91 ± 23	82 ± 13
	B	74 ± 21	89 ± 13	94 ± 20	95 ± 19

*i.e. shoot-length for Douglas-fir, needle length for ponderosa pine.

Table 18. Dry weights of new shoots of Douglas-fir and ponderosa pine under different acid treatments. Experiment 4(b). (Mean weights in grams ± standard deviations; n=12).

Species and seed source	Soil (both Shaver)	Treatment pH			
		2.0	3.0	4.0	5.6
Douglas-fir, 252	A	2.24 ± 0.77	1.64 ± 0.82	1.85 ± 0.78	1.90 ± 0.92
	B	1.89 ± 0.48	1.31 ± 0.58	1.99 ± 1.10	1.25 ± 0.37
Ponderosa pine, 310	A	1.77 ± 0.70	1.85 ± 0.69	1.76 ± 0.50	1.78 ± 0.50
	B	1.70 ± 0.70	1.46 ± 0.57	1.50 ± 0.44	1.45 ± 0.55
Ponderosa pine, 531	A	1.75 ± 0.73	1.64 ± 0.51	1.94 ± 0.40	2.10 ± 0.68
	B	1.84 ± 0.49	1.81 ± 0.63	1.61 ± 0.55	1.81 ± 0.51
Douglas-fir (combined*)		2.06 ± 0.65	1.47 ± 0.71	1.91 ± 0.92	1.60 ± 0.78
Ponderosa pine (combined*)		1.77 ± 0.64	1.69 ± 0.60	1.70 ± 0.49	1.78 ± 0.59

*i.e. irrespective of seed source or soil sample

GENERAL DISCUSSION

From the separate experiments conducted in this project, a number of principles and general results emerge. Severe acid treatments (pH 3.0 to 2.0) caused decreases in productivity of both above-ground and below-ground portions of selected agricultural crop species. Such crop-productivity decreases are most pronounced on more-fertile soils or those that have received fertilizer-salt applications. Thus, in the most productive areas of the State there is the possibility of crop damage by acid rain.

However, a number of mitigating circumstances also exist that modify this conclusion making the possibility less-alarming. Firstly, most of the highly-productive areas of the central-valley agricultural areas of California are intensively-managed; irrigation and application of ferti-lizer-salts are common. Such management practices would probably far ex-ceed the effects of acidic depositions from the atmosphere, modifying their effects by dilution or neutralization. Secondly, the main agricul-tural areas do not receive very much rain, whether it be acidic or not. However, dry atmospheric precipitation in these areas may be appreciable. To date, little research has been conducted on quantifying such dry de-position, or studying effects on plant productivity and quality. Accumu-lated dry acidic material on plant leaves or fruit may prove to be as damaging as direct contact by wet acid-rain, particularly where fog or high humidity is common.

In the less-fertile soils, where crop-productivity is limited be-cause of nutrient deficiencies, particularly those of nitrogen and/or sulfur, productivity may actually be increased by acidic atmospheric in-puts. This research has documented increases in growth of clover, barley,

cabbage and sugar-beet with increases in acidity down to pH 3.0, although in most cases further acidity (to pH 2.0) decreased growth. These results suggest that modest increases in atmospheric acidity stimulated plant growth because of the addition of nitrogen and sulfur which are in limited supply in poorer soils.

At the same time, however, other effects of acid-rain are detrimental to plants. Although productivity may increase with modest increases in acidity, plant quality may decrease. Leaves and fruit may be spotted or discolored by acid rain, rendering the plant product less-desirable for marketing and consumption. In this research, removal of the protective wax-covering of leaves by acid rain was documented, even though total plant productivity was enhanced. Such damage may also lead to subsequent insect or fungal attack, although these effects were not specifically studied here.

Increases in plant productivity with increasing acidity does not occur without cost, which, on the long-term basis may outweigh short-term benefits. This is illustrated by effects on the soil, and highlights the importance of recognizing the interactions between acid rain depositions, plant growth, and the soil in which the plants are growing. In all cases, whether or not the soil received fertilizer-salts, the acidity of the soil increased. Such increases in soil acidity result in the release of important plant nutrients as well as the mobilization of toxic elements such as manganese and aluminum. If circumstances are such that plants are not present to absorb these available nutrients, they could then be leached from the soil to streams and groundwaters. This would be a net loss to the soil resource, and in the case of toxic elements would pose a threat to the quality of the aquatic system, including fish which are quite

sensitive to increases in the concentration of aluminum. Thus, it must
be stressed that results of this research indicating increased plant growth
by acid rain inputs must be balanced against these possible detrimental
effects of soil leaching and increased elemental concentrations of drain-
age waters.

Results of this research also clearly demonstrate that plant response
to acid treatments vary due to the complex interaction of the soil-plant
system with inputs of all substances in the atmospheric input. Thus, re-
search on plant sensitivity to acid rain should not be restricted to plants
where the characteristics of the soil in which they are growing are either
unknown or ignored.

Results on a short-term basis have also been obtained for important
tree species of California. Germination tests using seed of Douglas-fir
and sugar pine indicate that germination is not inhibited at acidity levels
experienced in the field, but early growth of young seedlings is inhibited
by severe acidic treatment (pH 2.0). Similarly, growth of two-year-old
Douglas-fir and ponderosa pine showed little deleterious effects during
short-term experiments, except in the severe treatments. At extreme acid-
ity, new-season needles developed brown spots and seedlings wilted. How-
ever, these short-term experiments are not indicative of what might occur
in a cumulative manner over many years in the field. Although deleterious
effects on tree species were minor over one season's growth, over many
years productivity could be decreased, both because of direct effects on
the foliage, and because of decreases in soil fertility due to small but
cumulative leaching of soil nutrients.

California forests, unlike agricultural areas, do not lend themselves
to ameliorative management practices on a large scale; this is an addition-
al point indicating that potentially sensitive and susceptible areas of

California to damage by acid rain, are the foothill and forested areas, especially in the Sierra Nevada.

The sensitivity of granitic, forested soils of the Sierra Nevada was also demonstrated in this research project by a series of soil-leaching experiments using a wide array of soils from California. Soil sensitivity to acid rain can be described in terms of (a) the amount of depletion of the soil nutrient capital, or (b) the amount of nutrients and toxic elements leached to drainage waters. Tests using soils along a transect from the foothills up to the ridge of the Sierra Nevada, indicate that soils of the higher elevations are most sensitive. These soils are typically of minimal depth and degree of development, and are subject to high amounts of precipitation. Geographically, they are located in areas near the tree-line which are used as water-catchments and contain many lakes that are oligotrophic (i.e., relatively nutrient poor). Thus, leaching of nutrients and other elements such as aluminum from these areas not only poses a threat to depletion of soil nutrients, but also poses a threat to water quality and to aquatic life. The high-elevation forests are almost impossible to ameliorate once damaged. Cumulative effects, even of a subtle nature from year to year, are likely to be long-lasting. Thus, areas of the Sierra Nevada which lie in the general area of wash-out of air-pollutants from metropolitan areas are likely to receive greatest impacts; these mountainous areas are also most-difficult to ameliorate. Future research should therefore be centered on the soils, forests and water-resources of these areas.

REFERENCES

Abrahamsen, G., Bjor, K., and Olav, T. 1975. Field experiments with simulated acid rain in forest ecosystems. Research Report 4-76, 15 pp. SNSF-project, 1432 As-NLH, Norway.

Barrett, E., and G. Brodin. 1955. The acidity of Scandinavian precipitation. Tellus 7: 251-257.

Bergseth, H. 1975. Verdrangung von magnesium und calcium in Waldboden dusch hydrogenionen. Acta Agric. Scand. 25: 225-230.

Cogbill, C. V., and G. E. Likens. 1974. Acid precipitation in the northeastern United States. Water Resour. Res. 10: 1133-1137.

Cole, D. W., Crane, W. J. B. and Grier, C. C. 1975. The effect of forest management practices on the water chemistry in a second-growth Douglas-fir ecosystem. Forest Soil and Land Management. Proc. 4th N-American Forest Soils Conf., Quebec. Bernier, C. and Winget, C. H. (eds.). Les Presses de l'Universite Laval, Quebec pp. 195-208.

Cowell, D. W., A. E. Lucas and C. D. A. Rubec. 1981. The development of an ecological sensitivity rating for acid precipitation impact assessment. Lands Directorate Environment Canada. Working Paper No. 10, 42 p.

Cowling, E. B., and R. A. Linthurst. 1980. Research on effects of acid precipitation on aquatic and terrestrial ecosystems. USEPA-NCSU, Acid Precipitation Program, 1st Ann. Report, 90 p.

Dochinger, L. S. and Seliga, T. A. (eds.). 1976. Proc. of the 1st Int. Symp. on Acid Precipitation and the Forest Ecosystem. For. Exp. Stn., Upper Danby, PA. USDA For. Serv. Gen. Tech. Ref. NE-23. 1074 p.

Drablos, D., and A. Tollan (eds.). 1980. Ecological impact of acid precipitation. Proc. Intern. Conf., Sandefjord, Norway, March 11-14, 1980, SNSF project, Oslo. 383 p.

Evans, L. L., Gmur, N. F., and Da Costa, F. 1977. Leaf surface and histological perturbations of leaves of Phaeolus vulgaris and Helianthus annus after exposure to simulate acid rain. Amer. J. Bot. 64: 903-913.

Holmgren, G. G. S., R. L. Juve, and R. C. Geschwender. 1977. A mechanically controlled variable rate leaching device. Soil Sci. Soc. Am. J. 41: 1207-1208.

Hutchinson, T. C., and M. Havas (eds.). 1980. Effects of acid precipitation on terrestrial ecosystems. Plenum Press, New York. 654 p.

Interagency Task Force on Acid Precipitation, 1981. National Acid Precipitation Assessment Plan. Jan. 1981 draft. Council on Environ. Quality, Wash. D.C., 129 p.

Jenny, H., S. P. Gessel and F. T. Bingham. 1949. Comparative study of decomposition rates of organic matter in temperate and tropical regions. Soil Science 68: 419-432.

Johnson, D. W. and Cole, D. W. 1977. Anion mobility in soils. Relevance to nutrient transport from terrestrial to aquatic ecosystems. Ecological Research Series, EPA-600/3-77-068. Environ. Protection Agency, Oregon. 27 p.

Jonsson, B. and Sundberg, R. 1972. Has the acidification by atmospheric pollution caused a growth reduction in Swedish forests? A comparison between regions with different soil properties Skogshogskolan. Inst. Skogprod. Rapporter och Uppsatser. No. 20, 48 pp.

Kuehn, M. 1972. Acid rainfall and conifer seedlings. M.S. thesis.

Colorado State Univ., Fort Collins, CO., 81 p.

Lee, J. J., G. E. Neely, S. C. Perrigan and L. C. Grothans. 1980. Effect of simulated sulfuric acid rain on yield, growth and foliar injury of several crops. Tech. Pap. 5544, Agric. Expt. Sta., Oregon State Univ., Corvallis, OR., 30 p.

Likens, G. E. 1976. Acid precipitation. Chem. Eng. News 54: 29-44.

Likens, G. E., R. F. Wright, J. N. Galloway, and T. J. Butler. 1979. Acid Rain. Sci. Am. 24L: 43-51.

Liljestrand, H. M., and J. J. Morgan. 1978. Chemical composition of acid precipitation in Pasadena, CA. Environ. Sci. & Tech. 12: 1271-1273.

McColl, J. G. 1980. A survey of acid precipitation in northern California. Final report, California Air Resources Board. University of California, Berkeley. 94 p.

McColl, J. G. 1981. Increasing hydrogen ion activity of water in two reservoirs supplying the San Francisco Bay area, California. Water Resourc. Res.(in press).

McColl, J. G. and Cole, D. W. 1968. A mechanism of cation transport in a forest soil. Northwest Sci. 42: 134-140.

Morgan, J. J., and H. M. Liljestrand. 1980. Measurement and interpretation of acid rainfall in the Los Angeles basin. Final Report, CARB, 54 p.

Nie, H. N., C. H. Hall, J. G. Jenkins, K. Steinbrenner, and D. H. Bent. 1975. Statistical package for the social sciences. 2nd. Ed. McGraw-Hill, N.Y. 675 p.

Overrein, L. N. 1972. Sulphur pollution. Patterns observed. Leaching of calcium in forest soils determined. Ambio 1: 145-147.

Overrein, L. N., H. M. Seif, and A. Tollan. 1980. Acid precipitation-

effects on forest and fish. Final Rep. of SNSF project, 1972-1980. SNSF-project Res. Rep. FR 19/80, Oslo, Norway, 175 pp.

Perry, E. P., P. J. Zinke and J. R. Heater. 1964. Some relationships between cation exchange capacity and carbon content of soils under forest vegetation in California. Proc 3th. Intern. Congr. Soil Sci., Bucharest, Romania. Trans. Comptes Rendus Berichte Vol. 3: 363-376.

Shriner, D. S., C. H. Abner, and L. K. Mann. 1977. Rainfall simulation for environmental application. Oak Ridge Nat. Lab., Enviro. Sci. Div., Pubb. Ns. 1067, 17 pp.

Tollan, A., and L. N. Overrein (eds.). 1978. Annotated bibliography 1974-1977, SNSF project; Acid precipitation-effects on forest and fish. SNSF, Oslo, Norway. 39 p.

Tveite, B. 1975. Acid precipitation-forest productivity. Regional tree-ring width survey. SNSF-project, TN 11/75, 49 pp., Norway.

USDA Forest Service. 1974. Seeds of woody plants in the U.S. Schopmeyer, C. S. (Tech. Coordinator). Agric. Handbook #450.

Wilklander, L. 1973. The acidification of soil by acid precipitation Grundforbattring 26: 155-164.

Wilklander, L. 1975. The influence of anions on adsorption and leaching of cations in soils. Grundforbattring 27: 125-135.

Wilklander, L. and Anderson, A. 1972. The replacing efficiency of hydrogen ion in relation to base saturation and pH. Geoderma 7: 159-165.

KEY TO SYMBOLS AND ABBREVIATIONS

Units of measurement:

μeq	microequivalent
ml	milliliter
l	liter
cm	centimeter
m	meter
km	kilometer
g	gram
kg	kilogram
μmho	micromhos
ha	hectare

Chemical symbols:

H	hydrogen		N	nitrogen
C	carbon		Cl	chloride
O	oxygen		CO_2	carbon dioxide
Na	sodium		HCO_3	bicarbonate
K	potassium		NH_4	ammonium
Ca	calcium		NO_3	nitrate
Mg	magnesium		SO_4	sulfate
Fe	iron		HNO_3	nitric acid
Mn	manganese		H_2SO_4	sulfuric acid
Cu	copper		HCl	hydrochloric acid
Zn	zinc		H_2CO_3	carbonic acid
S	sulfur		C.E.C.	cation exchange capacity

Superscripts (e.g., Mg^{2+}) indicate ion charge and valence.

Square brackets (e.g., $[Mg^{2+}]$) indicate ion concentration.

pH, a measure of acidity = $-\log [H^+]$.

Statistical symbols:

n	sample number
r	simple correlation coefficient
r^2	coefficient of determination
$\bar{X}$	mean
S.E.	standard error of mean
α	alpha value, or probability level
*	5% probability level
**	1% probability level
***	0.1% probability level
Σ	sum

APPENDIX 1. <u>Analytical Methods</u>

A. PLANTS

<u>Plant Dry Weight</u>

Immediately after harvesting, plants are placed in individual brown paper bags and put in an oven at 70° C overnight. This dried plant material is then removed from the bag and weighed on an analytical balance.

<u>Plant digest for metals</u>

50 mg of dried plant material is boiled in a 5:1 mixture of nitric:perchloric acid then cooled and diluted to 50 ml. This digest is then analyzed for Na, K, Ca, Mg, Fe, Zn, Cu and Mn by atomic absorption.

References: Johnson, Clarence M., and A. Ulrich. 1959. Analytical methods for use in plant analysis. pp. 32-33. California Agricultural Experiment Station Bulletin 766.

Varian Techtron. 1972. Analytical methods for flame spectroscopy.

<u>Total Plant Nitrogen</u>

50 mg dried plant material, 0.5 g of a 2/25 w/w H_gO and K_2SO_4 mixture and 1.5 ml of concentrated acid are combined in a Kjeldahl flask, heated gently for a few hours till frothing ceases, then

strongly until the solution clears. The digest is then cooled and rinsed out into a volumetric flask, made to 50 ml and poured into a beaker. A NH_3 electrode is inserted, the solution stirred with a magnetic stirrer and 0.5 ml of 10$\underline{M}$ NaOH and Kl added. A reading is taken after one minute and 0.5 ml of 0.250N NH_4Cl added as a standard addition and another reading taken after one minute.

All plant nitrogen is assumed to have been converted to NH_4^+. Total plant nitrogen is calculated from the NH_4^+.

Total Plant Phosphorous

0.5 of dried plant material is wet ashed by boiling in a 5/1 mixture of concentrated nitric and perchloric acid for several hours, then cooled and diluted to 50 ml. A 20 ml aliquot is taken and acidified with 1.8 ml of perchloric acid, then 2 ml of an amidol reagent and 1 ml of 8.3% ammonium molybdate are added in that order. The resulting solution is made to 25 ml and the transmittance read at 660 mμ after 5 but within 30 minutes. Standards are prepared in a similar manner.

Reference: Johnson, Clarence M., and Albert Ulrich. 1959. Analytical methods for use in plant analysis. pp. 52-53. California Agricultural Experiment Station Bulletin 766.

Total Aluminum in Plants

Plant material digested for metal analyses (previously described) is used. Aluminum is then determined, using the same method described under the heading "aluminum in soil."

Total sulfate in plants

Plant material was digested as in the analysis of major cations in plant material. 10 ml of this digest was transferred to an erlenmeyer flask and mixed with 10 ml of water, 1 ml. of barium chloride-gelatin reagent was added, the mixture swirled and allowed to stand. After 40 minutes the mixture was transferred to a Klett-Summerson colorimeter cell with a 2 m light path and the turbity measured on a Klett-Summerson photoelectric colorimeter fitted with a blue (no. 42) filter. Readings were compared to appropriate standards made from K_2SO_4.

Reference: Tabtabai, M. A., J. M. Bremner. 1970. "A simple Turbidimetric Method of Determining Total Sulfur in Plant Materials." Agronomy Journal Vol. 62 p. 805-806.

Scanning electron microscopy

Leaf-pieces, 1 cm^2, were cut from the oldest healthy leaf at harvest, then immediately frozen in freon cooled with liquid nitrogen and dried under high vacuum. The freeze-dried material was then coated with 300 A of gold-palladium, and examined with a Coates-Wetter field emission scanning electron microscope.

Reference: Dawes, C. J. 1979. Biological techniques for transmission and scanning electron microscopy. Ladd Research Industries, Inc. Burlington, Vt.

B. SOILS

Cation Exchange Capacity of Soil

A soil extractor manufactured by: Concept Engineering, Inc.
1800 Center Park Road
South Industrial Park
Lincoln, Nebraska 68502

is used in this analysis. It is capable of extracting 24 samples

at once.

2.5g of soil per sample is leached overnight with 60 ml of pH

7.0 NH_4Ac and the filtrate saved for analysis of major cations. The

soil is then leached twice with 60 ml of ethanol to remove non-exchange-

able NH_4^+, and then overnight with 60 ml of acidified 10% NaCl to remove

exchangeable NH_4^+. This NaCl extract is analyzed for NH_4^+ with an ammonia

electrode. The amount of exchangeable NH_4^+ released is considered to

be equal to the cation exchange capacity of the soil.

References: Black, C. A. 1965. Methods of Soil Analysis. pp. 891-899.
American Society of Agronomy, Inc., Madison, Wisconsin.

Major Cations and Base Saturation of Soil

The NH_4Ac extract described under the heading "Cation Exchange

Capacity" is analyzed for the major cations Na, K, Ca, and Mg by atomic

adsorption. The sum of these cations in meq is divided by the cation

exchange capacity to provide the base saturation of the soil.

Reference: Black, C. A. 1965. Methods of Soil Analysis. pp. 905-906.
American Society of Agronomy, Inc., Madison, Wisconsin.

Soil pH

10g of fresh soil is weighed out into a 50 ml beaker, 10 ml of deionized water added and the resulting slurry mixed thoroughly with a spatula. The sample is allowed to stand for two hours, then a magnetic stirrer is added and a previously standardized combination pH/reference electrode is inserted into the slurry. The meter is allowed to equilibrate for 5 minutes and a reading taken.

Aluminum in Soil

Extractable Al is measured by extracting 50g of moist soil with 250 ml of 1N KCl. Aluminum is determined by fluorescence by adding a solution of morin dye to the extract and measuring its emission at 500 nm with an excitation wavelength of 425 nm. At least several standard additions of Al are made to two samples in twenty to check for possible interferences.

References:

KCL Extract: Black, C. A. 1965. Methods of Soil Analysis. pp. 985, 988. American Society of Agronomy, Inc. Madison, Wisconsin

Al Fluorescence: Will, Fritz. 1961. Fluorometric determination of Al in the ppb range. Analytical Chemistry, 33:1360-62.

Manganese in Soil

Manganese is extracted by shaking 10 g of fresh soil with 20 ml of 0.005$\underline{M}$ DTPA for exactly two hours, then centrifuging and filtering

the resulting soil slurry. Manganese is determined by atomic adsorption on the resulting supernatant.

References: Lindsay, W. L. and W. A. Norvell. 1969. Development of a DTPA micronutrient soil test. Agron. Abstr., p. 84.

Soltanpour, P. N., A. Khan, and W. L. Lindsay. 1976. Factors affecting DTPA - extractable Zn, Fe, Mn, and Cu from soils. Commun. in Soil Science and Plant Analysis 7:797-821.

Nitrate in Soils

20g soil is shaken with 200 ml 2N KCl for one hour, then filtered through Whatman #42 filter paper and the filtrate refrigerated and saved for later analysis.

NO_3^- in the extract is determiend by diluting the extract 1:10 to 1:100, reducing to NO_2^- by addition of hydrazine sulfate, and measuring this colorimetrically by addition of sulfanilamide and napthlethylendiamine dehydrochloride.

References: Black, C. A. 1965. Methods of Soil Analysis. pp. 905-906. American Society of Agronomy, Inc. Madison, Wisconsin

and, Personal communication, Dr. Robert Leonard, Tahoe Research Group.

Exchangeable NH_4^+ in Soils

50g of soil is extracted with 200 ml of 1 N KCl, and made to 250 ml. The ammonia concentration is immediately measured with an ammonia electrode manufactured by Orion Research, 380 Putnam Ave. Cambridge, Mass.

Reference: Black, C. A. et al. 1965. "Methods of Soil Analysis."
American Society of Agronomy, Inc. Publisher, Madison,
Wisconsin, U.S.A. pp. 1185-1187.

Organic Carbon in Soil

10 ml of 1 $\underline{N}$ $K_2Cr_2O_7$ is added to 1g of air dried soil containing 10 to 25mg of organic C. The flask is swirled, 20 ml of concentrated H_2SO_4 added and the resulting mixture mixed thoroughly. The suspension is allowed to cool, 200 ml of H_2O are added and the mixture filtered through whatman No. 1 paper. 3-4 drops of)-phenantholine indicator are added and the solution titrated with 0.5 N $FeSO_4$ to a red endpoint.

Organic C is assumed to have been consumed by $K_2Cr_2O_7$ and calculated from the amount of $K_2Cr_2O_7$ not used.

Reference: Black, C. A. 1965. "Methods of Soil Analysis Part 2."
Agronomy Series, No. 9. pp. 1372. American Society of
Agronomy, Inc., Madison, Wisconsin.

Particle Size Analysis of Soil

40g of air dried soil is mixed in a blender for 5 minutes with a 5g/l solution of Calgon. The slurry is poured into a 1 l graduated cylinder, made to volume, mixed then left to stand and the time recorded. A hydrometer is

is immediately inserted in the cylinder, and readings are taken at 30 secs., 1 min., and also at approximately 7 and 10 hrs. The temperature of the solution is also measured at these times.

Using standard calibration tables, the amount of sand, silt and clay can be calculated.

Reference: Black, C. A. 1965. "Methods of Soil Analysis - Part 1". Agronomy Series, No. 9, pp. 562. American Society of Agronomy, Inc., Madison, Wisconsin.